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REPORTS

OF THE

PROGRESS OF APPLIED CHEMISTRY.

PLANT AND MACHINERY.

By W. H. Coleman, F.I.C,
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Owing probably to the general industrial depression, very little of great interest has appeared during the past year, which seems to have been devoted chiefly to minor improvements in existing plant and to investigations having for their object the collection of data which may serve as a basis for improving the design, working, and efficiency of various types of chemical plant. There is still room for a great deal of research in this direction and the joint action of the Association of British Chemical Manufacturers and the British Chemical Plant Manufacturers' Association in forming a Committee to consider the standardisation of chemical plant will, it is hoped, lead to results of great benefit to the industry, not only by rendering various types of plant uniform in design and construction and facilitating output, but also—and this is perhaps more important in some respects—enabling broken parts to be replaced from stock. This would do away with many serious delays to the course of production due to the breakdown of machinery.

Taking the subject in as natural an order as possible, the production of power forms a useful starting point. Although the coal strike in the earlier part of the year forced many manufacturers to replace their coal-fired boiler furnaces by arrangements for the utilisation of liquid fuel, nothing very novel in the shape of oil burners has appeared. Perhaps the most important contribution to our knowledge was P. Kestner's lecture on boiler-feed water.[1] The corrosion of boiler plates has been shown to be very largely due to oxygen dissolved in the feed water; it was further shown

[1] P. Kestner, *J.*, 1921; 67T.

that this could be got rid of by passing the water, on its way to the boiler, through vessels filled with turnings made from iron containing a good deal of manganese and which was easily oxidised. This process is combined with a system of continuous blowing down and utilisation of the heat of the water blown down so that both corrosion and accumulation of sludge in the boiler are avoided.

In grinding and pulverising plant many minor improvements have been effected which, however, do not require individual mention, and the same may be said to a large extent of mixing and agitating machinery.

However, in a paper on the manufacture of pure hydrogen[2] some interesting particulars of plant occur. Purifiers for both water-gas and hydrogen were successfully constructed of reinforced concrete and the vessel used for the hydrogenation of oils, in which a very intimate mixture of the gaseous and liquid materials is essential, has some features well worthy of consideration. It consists of a tall, relatively narrow cylinder, suitably jacketed and expanded above and below into chambers of greater diameter. The narrow cylinder is provided with fixed transverse baffles shaped like propeller blades, each alternate baffle being arranged to direct the gas and liquid, which are circulated in opposite directions by external pumps, alternately in a clockwise and an anti-clockwise direction. The advantage of such apparatus consists in providing means for obtaining an intimate contact without the use of any mechanically-operated devices, and which can consequently be constructed of almost any suitable material. This type of plant should find many applications in other directions than that for which it was designed.

The use of superheated water and of a high-boiling and high-flash-point oil for conveying heat from the furnace to the vessel to be heated is attracting more attention and presents several features of importance, notably the ease of control which such a system gives in addition to the lessening of fire risks. It has also been proposed[3] to utilise superheated steam for heating by spraying the solution which it is desired to heat into the steam. In this way very intimate contact is obtained and the steam becomes saturated. The operation is so controlled that the saturated steam obtained is at sufficient pressure for use after being separated from the concentrated liquid.

A study of the condensable gases in ammonia refrigerating machines,[4] which consist chiefly of nitrogen and hydrogen, together with a little oxygen, has led to the conclusion that the presence of carbonates, acetates, and acetonitrile serves to increase considerably

[2] E. B. Maxted, *J.*, 1921, 171T.

[3] R. Kaesbohrer, G. P. 336,611; *J.*, 1921, 614A.

[4] E. C. McKelvy and A. Isaacs, *U. S. Bureau of Standards, Tech. Paper* 180; *J.*, 1921, 287A.

the corrosive action of ammonia at ordinary temperatures, but that less than 0·003% of carbonate is without action. The addition of 0·2% of sodium or potassium bichromate to tho charge prevents corrosive action. Advantage is taken of the disproportionately high value of the specific heat of air at very high pressures to utilise it in place of ammonia or carbon dioxide in refrigerating machines. The air is compressed to a very high degree and subsequently expanded to a lower but still high (50 atmospheres) pressure.[5]

In processes for purifying gases and condensing volatile vapours electrical precipitation methods havo received a good deal of attention chiefly as to details of construction. The capacity of activated carbon for absorbing the vapour of water, ether, alcohol, benzene, etc. has been determined, and useful curves constructed showing the relation between the amount of vapour absorbed and the partial pressure of the vapour in the mixture. Carbon is usoful for removing vapours of organic substances, but not for small traces of water.[6] Colloidal silica or silica gel is suggested as an absorbent for use in the recovery of gasoline, sulphur dioxide, nitrogen oxides, and vapours of volatile solvents.[7] A variety, prepared by drying the unwashed silica gel from water-glass and hydrochloric acid, at 300° C., plunging it while still hot into hot distilled water, washing by decantation till free from hydrochloric acid, drying again at 300° C., and repeating the process till a material free from chloride is obtained, gives a product which has an absorptive capacity for nitrogen at −190° C., about 63% greater than that of the best charcoal.[8]

Continuous, rotary filters seem to be finding an extended application in chemical industry, and filter cloths of metallic gauze, or of a mixture of metallic filaments with animal or vegetable fibres, are now used more frequently. Filter cloths are protected from corrosive action by coating them with a suitablo metal, either by spraying or by galvanic deposition, care of course being takon not to fill up the pores entirely.[9] Materials which contain colloidal matter and are difficult to filter are, if practically free from acid, rendered easy of filtration by the addition of a basic zinc compound.[10] This idoa of adding substances to assist in filtration should be capable of considerable extension and is worthy of further study. Improved filter-presses are constructed with wide, double

[5] Ges. für Lindes Eismaschinen A.-G., G. P. 323,950 ; *J.*, 1921, 171A.

[6] E. Berl and K. Andress, *Z. angew. Chem.*, 1921, **34**, 369, 377 ; *J.*, 1921, 567A.

[7] E. B. Miller, *Chem. and Met. Eng.*, 1920, **23**, 1155, 1219, 1251 ; *J.*, 1921, 109A.

[8] H. Briggs, *Proc. Roy. Soc.*, 1921, **A**, **100**, 88 ; *J.*, 1921, 799A.

[9] J. Rahtjen, G. P. 329,061 and 330,715 ; *J.*, 1921, 203A, 287A.

[10] D. P. Haynes, and Roseberry Surprise Mining Co., U.S.P. 1,373,887 ; *J.*, 1921, 334A.

inlets and outlets. The cloths are supported by wide-mesh, double-crimped, wire gauze sheets, supported by a few diagonal ribs cast on the face of the plate. This allows the filtrate to drain away freely and prevents the cloth bedding against the plate. Until the frames are full, only one inlet is used, the other serving to allow air to escape. The outlets for each face of the plate are arranged on opposite sides so that any leaky cloth can be located and shut off.[11] The Joint Committee referred to before, has issued a Report on the Standardisation of Filter-presses.[12] The details of construction of over 800 cast-iron presses have been collected and proposals for standardisation of dimensions and forms of construction have been drawn up and are being submitted for consideration. One fact which has been brought out is an excellent example of the advantages to be gained by the whole industry from the work of the Committee; it has been found that the provision of a flange on the side of the frame from which the washing liquid is discharged considerably increases the efficiency of the washing, as it prevents the liquid from passing round the edge of the cake without doing any work. Now this fact has been known for some time to many people, but only now, and owing entirely to the work of the Committee, has it been adopted as a standard feature of construction. Team work of this kind should do much to help the industry not only by facilitating construction and replacement of plant, but if it happily leads to a pooling of our knowledge of methods of construction and of manipulation it will set free much energy for the investigation of fresh fields instead of wasting it on rediscovering, over and over again, what has already been found out but not made public. Another probable advantage that will result from this work will be the simplification of the details of plant whilst retaining the guiding principles.

In drying plant, as in many other branches, the year has been prolific in investigations undertaken to obtain data for the furtherance of improved design and methods of operation.[13] The use of gases such as carbon dioxide and sulphur dioxide is advocated for drying certain colloidal substances such as smokeless powder.[14] The gas is circulated over the material, and in the case of smokeless powder takes up ether, and this is subsequently recovered by passing the gas through alcohol.

Another new departure is the application of the thermo-compressor system to drying. A drying kiln very similar to the well-known rotary roaster is constructed with hollow metal hearths; the steam given off by the material as it passes over the hearths is withdrawn,

[11] C. D. Burcheral, *Chem. and Met. Eng.*, 1921, **25**, 476; *J.*, 1921, 725A.
[12] *J.*, 1921, 401R.
[13] *J. Ind. Eng. Chem.*, 1921, **13**, 427; *J.*, 1921, 497A.
[14] G. P. Lunt, E. P. 159,465; *J.*, 1921, 726A.

and after having its temperature raised by being compressed, it is returned to the hollow hearths to serve as the heating agent.

Studies of evaporators have been continued,[15] and in evaporators having horizontal tubes it has been found that the heat transmitted from the superheat of superheated steam is small compared with that transmitted from the latent heat of condensation, also that the maximum capacity occurs when the tubes are from one-half to two-thirds submerged in the liquid. Other experiments with vertical evaporators concentrating tannin extract have shown that greater efficiency is attained where the heating surface diminishes in successive effects than in apparatus in which the effects are all of the same size or are in ascending order of size.[16] In evaporators working with steam compression (thermo-compressor systems) it has been found[17] that much steam is required to drive the compressors, and that this must be taken into consideration. With weak solutions, saving is only effected by linking the compressor to the first effect of the series, and with more concentrated solutions and higher pressures, steam compression offers no advantages.

Piston compressors are better than centrifugal compressors, but the oil carried forward with the compressed steam diminishes the heat transmission considerably.

The great importance of maintaining constant conditions in continuous distilling and fractionating plant is much too frequently ignored and the description of devices regulating pressure, temperature, and rate of feed[18] is of interest.

For the protection of vessels from corrosion metallic coatings applied galvanically have only a short life, owing to their porosity, and sheet metal linings are useless where vacuum is to be used, the only satisfactory metallic lining being homogeneous lead. Paint and varnish will not withstand mechanical friction and enamel, though otherwise very good, chips easily. Earthenware linings are good but too thick and heavy, and linings formed of thin glass plates have been found to be very durable and not liable to fracture when exposed to sudden changes of temperature.[19] A mixture of 40 parts of sulphur with 60 parts of sand melted together and poured into moulds like concrete is a useful material for the construction of acid tanks and gutters, etc. When set it has a tensile strength of 400 lb. to the square inch, and it can be poured in several separate lots, as each fresh lot melts the surface of the previous one and forms a good joint.[20]

[15] W. L. Badger, *Chem. and Met. Eng.*, 1921, **25**, 458 ; *J.*, 1921, 725A.

[16] Depasse, *Bull. Assoc. Chim. Sucr.*, 1921, **38**, 383 ; *J.*, 1921, 681A.

[17] H. Claassen, *Z. angew. Chem.*, 1921, **34**, 233 ; *J.*, 1921, 455A.

[18] E. Barbet et Fils et Cie., E. P. 129,648 ; *J.*, 1921, 33A.

[19] F. Schüler, *Chem.-Zeit.*, 1921, **45**, 315 ; *J.*, 1921, 421A.

[20] R. F. Bacon and H. S. Davis, *Chem. and Met. Eng.*, 1921, **24**, 65.

A slide rule for calculating the wet and dry weights of damp material [21] and alinement charts or nomograms [22] are useful aids to the works manager, and their adaptation to other types of calculation ought not to present any great difficulty.

The question of corrosion of the materials used in the construction of chemical plant is of perennial interest, and the sudden and often inexplicable failure of lead sheets, specially those used in acid chambers, is unfortunately only too familiar. It is therefore of interest to refer to some work on this subject.[23] The study of etched surfaces of lead under the microscope has revealed that lead which has given way shows certain segregations in its crystalline structure, and although the work is being continued, at present Pattinsonian is to be preferred to Parkes lead, as the latter may contain dangerous amounts of zinc which are difficult to detect with the microscope.

The use of pumps and pipe lines for moving easily melted solids, such as salty creosote and pitch, and of motor trucks and tractors in chemical works, is extending,[24] and those requiring to employ safety devices against dangerous gases will find useful hints in the paper on industrial respirators.[25]

A very useful material for constructional work in chemical factories is the new heat-intercepting glass. This material contains small amounts of certain metals such as cerium, chromium, etc., which render the glass impervious to heat rays, whilst the light rays are not seriously impeded in their passage. It can be produced in several qualities, among which the "Aqueduct wire glass," which is drip-proof, should be very suitable for roof lights over open evaporating and boiling pans, any moisture that condenses on the under surface being guided by grooves formed in the under side of the glass to a gutter. Another useful kind is the "Corrugated wire glass"; this can be used in conjunction with corrugated iron sheets to provide plenty of top or side light at little cost.[26]

One can hardly conclude without referring to the so-called "colloid mill," [27] though, as the reports received are somewhat conflicting, a reference will suffice.

[21] R. Scott, *J.*, 1921, 96T.

[22] A. J. V. Umanski, *Chem. Trade J.*, 1921, **68**, 233, 269; *J.*, 1921, 169A.

[23] W. G. McKellar, *J.*, 1921, 137T.

[24] S. P. Miller, *J.*, 1921, 153T, and W. P. Kennedy, *J.*, 1921, 271R.

[25] L. Levy and D. W. West, *J.*, 1921, 234T.

[26] G. Alleman, *J.*, 1921, 241T.

[27] B. Block, *Z. angew. Chem.*, 1921, **34**, 25; *J.*, 1921, 169A. H. Plauson, *ibid.*, 1921, **34**, 469, 473; *J.*, 1921, 799A.

FUEL.

By J. S. S. Brame,

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Coal.

J. E. Hackford[1] puts forward interesting speculations as to the conditions under which oil and coal were formed. In the case of a deposit containing either animal remains or marine vegetation, these on decomposition form oil and gas which, if in a sandy bed, are swept away by either gravity or water as rapidly as formed, since neither the animal remains nor the marine vegetation contain cellulosic material capable of forming a sponge-like mass, which would hold the oil *in situ* during the decomposition stage.

In the case of a buried deposit of terrestrial vegetation, similar decomposition would take place, but owing to the cellulosic nature of the material and its spongy character, the oil is retained while decomposition proceeds. With a rise of temperature not above 100° C. the oxy- or thioasphaltenes simultaneously formed with the oil are converted into kerotenes (those portions of bitumen insoluble in carbon bisulphide). The kerotenes become more and more insoluble, until they are not dissolved by pyridine or quinoline, and so remain as a solid in the sponge-like mass afforded by the cellulosic structure of the terrestrial vegetation. The amount of soluble bitumens should, therefore, be greatest in peat and should decrease through lignite, sub-bituminous, bituminous, and semi-bituminous coals, which is stated to be the case.

"Petroleum oils are clearly not derived from coal; but given a quantity of vegetal matter, petroleum may be produced under a given set of circumstances if no cellulose is present and coal will be formed if the vegetal matter contains sufficient cellulose to form a sponge."

F. Fischer and H. Schrader[2] consider also that hydrocarbons are formed from bitumen. The cellulose is decomposed by bacterial agency into carbon dioxide and water—a change which can be followed in peat. The cellulose disappears whilst the lignin of the vegetal matter is converted into those wonderfully indefinite "humic substances." It is claimed that the behaviour of cellulose and lignin respectively with reagents, and the production of phenols

[1] *Min. & Met.*, 1920, No. 163.

[2] *Brennstoff-Chem.*, 1921, 2, 37; *J.*, 1921, 172A.

from this portion of the coal substance, indicating that the benzene type of structure in lignin persists, show that lignin must be regarded as the mother-substance in coal. By concentration the waxes and resins in the vegetal matter become increased in the coal.

Mineral Matter in Coal.

F. S. Sinnatt, A. Grounds, and F. Bayley[3] presented an interesting paper on the white (or nearly white) partings of mineral matter, ranging in thickness from a mere film to one-eighth of an inch, which are frequently found in coal. It is found that these frequently show "rust," due to oxidation of ferrous iron; manganese was also shown to be a frequent constituent. These partings ("ankerites") are either substituted calc spar or dolomitised siderite, and have presumably been formed by the infiltration of water. They play an important part in the disintegration of coal, forming planes along which cleavage is easy. The coal substance may be very low in ash, and the analysis of the ash very different from that of the ankerites, the latter containing no alumina, whilst the silica content of the true coal ash is many times greater than that of the ankerites.

H. F. Yancey and T. Fraser[4] have extended the work on the sulphur in coal and investigated the important question of the distribution of the pyritic and organic sulphur. Sulphate sulphur was disregarded, being very low in freshly mined coal. Pyrites is very unevenly distributed and, depending on the form, more or less removed by coal washing. The organic sulphur varies in different coals over very wide limits. In ten coals it ranged from 20·4% to as high as 83·7% of the total sulphur. The ordinary washing processes do not remove organic sulphur, this being part of the coal substance, and when sulphur content in this form is high it limits seriously the extent of sulphur removal by washing. The distribution of organic sulphur is nearly uniform throughout the seam, and high pyritic sulphur content is not indicative of high organic sulphur. No evidence was found of any concentration of organic sulphur in the coal immediately adjacent to pyrite deposits.

A useful development in the activities of the Fuel Research Board is the issue of technical papers. In the first of these T. Gray and J. G. King[5] describe a new laboratory method for the assay of coal for carbonisation purposes. The main object, according to the text, was the development of a standard method of carbonisation assay, by means of which coals could be characterised and classified with a precision which has not hitherto been attained by any method in general use. It is questionable how far the results of carbonising 20 g. of coal up to a maximum temperature of 600° C.

[3] *J.*, 1921, 1T.
[4] *J. Ind. Eng. Chem.*, 1921, **13**, 35; J., 1921, 110A.
[5] *Cf. J.*, 1921, 205A.

throws light on results or characteristics which obtain at temperatures of more than double this maximum. For example, the highest gas yield is equivalent to 3560 cub. ft. (at 60° F.), and the "oils" have a maximum of 39 galls. per ton. Taking the minimum "oils" from bituminous coals (omitting a weathered sample) about 29 galls. per ton is recorded. Complete analyses of the gases evolved are tabulated; with three bituminous coals with approximately 40% of volatile matter (on ash-free dry coal), the carbon dioxide content of the gas is 10·4–13·7%, whilst with four other coals, volatile matter 37·25–38·28%, the carbon dioxide is only 4·2–7·5%. The evolution of carbon dioxide from lignites at low temperatures, as recorded by W. A. Bone (*loc. cit.*), is of interest in this connexion. It would have been interesting to have compared the oxygen content of the coal with the carbon dioxide in the gases, but unfortunately, complete as the data for the coal and products are in other respects, ultimate composition is not given. Such data would again have been useful in connexion with the yield of ammonia.

A method for determining the volatile matter in coal has been described by W. A. Bone and L. Silver[6] for which greater accuracy is claimed than is attainable by the standard American method, or by coking in a fireclay crucible heated in a muffle. The failure of these methods to indicate small differences in composition of anthracite through a seam led to the development of the new method, for details of which the original paper should be consulted. The special points claimed for the new method are accurate control of temperature and of the rate of heating, complete carbonisation at whatever working temperature is chosen, and carbonisation in an inert atmosphere.

Spontaneous Heating of Coal.

The Final Report of the Departmental Committee on Spontaneous Combustion of Coal in Mines[7] contains five sections: (1) Historical review, (2) Probable causes, (3) Practical aspect as applied to coal mines, (4) Hydraulic stowage, (5) Conclusions and recommendations. It cannot be said that the findings add in any way to what was general knowledge among scientific men who had followed the many researches on the causes. It is, however, useful to have this collection of historical material and the definite laying of the bogey of pyrites as the cause of combustion. It is interesting to compare the statement in Percy's "Metallurgy" (1875) with the Committee's conclusion. "Incipient combustion . . . was due to the heat developed by the oxidation of accumulated fine coal, just as in the well-known case of a heap of oil rags" (Percy).

[6] *Chem. Soc. Trans.*, 1921, **119**, 1145; *J.*, 1921, 615A.
[7] *Cmd.* 1417, 1921.

"The self heating of coal is mainly due to the absorption of oxygen by the coal resulting in the generation of heat . . . in so far as the heating effects are concerned [it] is a chemical process and not a physical process" (Report).

It may perhaps be well to quote the paragraph in the Report referring to pyrites: "Some small amount of heat may be developed by the oxidation of pyrites in the coal when it occurs in the form of marcasite; but that as pyrites is present in the coal in such small proportion as compared with the coal substance proper—which is a bad conductor of heat—the effect of this heat is negligible. The chief part played by pyrites when present in an unstable form is that of a disintegrator of the coal, so rendering the latter more permeable by air and exposing a greater area of coal substance to oxidation." This might almost be a quotation from the conclusions of the late V. B. Lewes.

T. F. Winmill[8] instanced an interesting case where pyrites did appear to have played an initial part in starting heating. The coal (Bullhurst, W. Staffs.) has such a low rate of heating when pure or when containing its usual amount of pyrites that it could not self-heat, yet the coal from the seam is more liable to spontaneous combustion than any other coal in the district. It does, however, contain patches of high pyritic content in a finely divided state and Winmill considers that the "initial impulse to self-heating" lies in these patches.

In one of the Appendices R. V. Wheeler describes experiments on the rates of oxidation of pyritic and non-pyritic coals which show that the presence of pyrites actually exerts a retarding action, probably acting in the same manner as any other inert material. The experiments were carried out in the apparatus Wheeler used for measuring rate of oxidation and relative ignition temperatures of coals.[9]

The following results, as c.c. of oxygen absorbed per gram of coal in 96 hours, were obtained :—

	Barnsley Seam.		Bullhurst "Billies."	
Temperature.	FeS_2 7%	FeS_2 17%	FeS_2 5%	FeS_2 36%
30° C.	3·94	3·61	2·00	1·28
100° C.	59·90	42·70	27·20	24·00

[8] See *Ann. Repts.*, 1917, **2**, 20.

[9] *Chem. Soc. Trans.*, 1918, **114**, 951; *Ann. Repts.*, 1919, **4**, 23.

Coal Cleaning.

This very important question has been dealt with in papers and articles by R. Nelson[10], G. St. J. Perrott and S. P. Kinney[11] and F. B. Jones.[12]

The great deterioration in the quality of coal used for general industrial purposes—particularly "unscreened small"—in recent years has been a source of loss and trouble in many industries, particularly the gas industry and power plants. Sir George Beilby, in his comprehensive James Forrest lecture on "Fuel Problems of the Future," delivered before the Institution of Civil Engineers, June, 1921,[13] gave the following averages over thirteen weeks for the coal used by the Central Electric Supply Co. :—

	1914-1915 (Winter).	1920.
Calorific value, B.Th.U.	10,800	10,580
Ash, %	13·0	18·4
Price per ton	14s. 6d.	45s. 2d.

The 5·4% ash increase means rather more than 1 cwt. per ton. From other authentic records covering forty separate cases for coal supplied under the same designation, before and since the war, the average increase in the ash was no less than 63%. When it is remembered that with high ash the mere percentage increase is not the full measure of the losses entailed, that greater difficulties arise in getting the best out of the fuel, that clinkering troubles and the cost of disposal of ashes arise, that, in the total, an enormous expenditure of other fuel, of rolling stock, and of labour is entailed in hauling useless mineral matter about the country, it is obvious that the erection of more extensive installations of cleaning plants is both a commercial and a national necessity. It is estimated that of the 45 million tons of slack coal used for industrial purposes nearly 90% is unwashed.

A simplified washery plant, known as the "Rheolaveur," of Belgian design, has been described by R. Nelson.[14] It is claimed that the initial cost is low, as are also maintenance and running costs, there is economy of space as compared with most washers, and complicated mechanism being absent, control is easy.

[10] *Engineering*, 1921, **112**, 74.
[11] *Chem. & Met. Eng.*, 1921, **25**, 182 ; *J.*, 1921, 615A.
[12] *Proc. S. Wales Inst. Eng.*, 1921, **37**, 331, 368 ; *J.*, 1921, 759A.
[13] See *Engineering*, 1921, **112**, 26.
[14] *Engineering*, 1921, **112**, 74.

One of the difficulties with the older type of washer was with the very small coal and washery fines, and a great deal of attention has been given to the froth flotation process (Trent process). This has been dealt with by R. Nelson (*loc. cit.*), Bergott and Kinney (*loc. cit.*), and F. B. Jones (*loc. cit.*). As applied to smalls the material is crushed to pass a screen with about one-tenth inch aperture; it is then mixed with three or four times its weight of water, together with about 1lb. of tar oil, water-gas tar, or similar products, per ton, and the whole thoroughly agitated so that efficient aeration takes place. The aerated froth carries the coal particles to the surface where the mass is removed by paddles.

The process is not dependent on differences of specific gravity, so that material of much the same specific gravity can be separated. Interstratified coal can be cleaned, but it is important to note that pyrites is wetted by oil and so floats with the coal. The oil product should preferably give a low surface tension between it and the coal and a high surface tension between coal-water and oil-water.

One of the difficulties with all fine and wetted coal is the removal of water. With the flotation process water may be removed by vacuum filtration to about 10%; a kneading machine is claimed to reduce it to 5%.

Results for the cleaning of Derbyshire Hard Top coal were:—

	Weight.	Ash.	Fixed carbon.	Volatile matter.
Untreated	100	29·55	48·20	22·35
Clean coal	75·1	9·86	60·24	29·90
Rejected	24·9	82·45	2·75	14·80

Lignite.

Sir G. Beilby[15] noted the importance of lignite and brown coal as fuels, pointing out that although there may be 40–60% of water present, they are by far the cheapest source of thermal units. In 1920 the brown coal and lignite output was 143 million tons, or 11% of the total coal output. To this output Germany contributed no less than 111 million tons, and Beilby makes the following significant comment: "According to the extent to which Germany can meet her own requirements for heat and power by the development of lignite, peat and water power, the output of her coal mines will be free for export, and she will thus take a more important place in the markets of the world."

[15] James Forrest Lecture, *loc. cit.*

In important Colonies, Australia and Canada, where there are large deposits of brown coal, its full and efficient utilisation is being investigated. A Lignite Utilisation Board of Canada has been established and considerable experimental work carried out. The price of coal in the provinces of Manitoba and Saskatchewan has risen to such a point that the production of a suitable alternative fuel from the large lignite deposits in these provinces was first considered, development being on the lines of concentration to give the best quality of solid product, the gases and tars being left out of consideration.

Working for the Board, E. Stansfield has studied the carbonisation of low-grade lignite from S. Saskatchewan,[13] and as a result a suitable type of plant and method have been developed and plant capable of dealing with 200 tons per day partly erected. It has been found that a short carbonisation in thin layers gives a residue of practically the same calorific value as that obtained by carbonisation at the optimum temperature (575° C.). The retorts in the semi-commercial carboniser are long and narrow, inclined at an angle of 45°. Cast iron baffles run across the retorts, with a clearance under them of 0·5–1 inch. This arrangement ensures a steady slip of the crushed lignite in layers of suitable thickness through the retorts. It is of interest to note the use of carborundum slabs for the bottom of the retorts—a use for high-temperature work which appears to be extending, for carborundum is also used in the low-temperature retorts in the Smith process (see p. 22).

The lignite is very poor, but the results of carbonisation give a fuel of quite good value, though high in ash :—

	Raw lignite.	Carbonised 3 mins. at 600° C.
Moisture, %	31·8	0·0
Ash, %	5·2	18·8
Volatile matter, %	28·9	13·2
Fixed carbon, %	34·1	68·0
B.Th.U. per lb.	4,260	11,180

The yields given are, per 2000 lb. of lignite charged : Gas, 3130 cub. ft. (385 B.Th.U. per cub. ft.) ; tar, 5·3 Imp. galls. ; ammonium sulphate, 10·2 lb. ; carbonised residue, 910 lb

[13] *J. Ind. Eng. Chem.*, 1921, **13**, 21; *J.*, 1921, 111A.

L. M. Thompson[17] gave an account at the Annual General Meeting in Montreal of the briquetting of the carbonised residue. The residue, because of its porosity, was found to require a much higher proportion of binder than for coal. Coal tar pitch was ultimately selected, 13 parts by weight being used for every 100 parts of carbonised residue.

E. P. Schoch[18] gives some details of the carbonisation of Texas *lignite*. This contains 32–40% of non-combustibles, several per cent. *being carbon dioxide.* On retorting at 525° C. the gas contained 23–33% of carbon dioxide; by the removal of this down to some 2% the calorific value of the gas was raised to approximately that of good coal gas. Neither the Texas nor Saskatchewan lignite yielded anything approaching the 10,000 cub. ft. of gas per ton, which has been mentioned by some writers. This high figure has been the result of high moisture acting on carbon under different carbonising conditions.

W. A. Bone[19] records the production at low temperatures of gas which consists largely of carbon dioxide, with some carbon monoxide, methane, and nitrogen. Concentration ("upgrading") occurs, and Bone suggests the improvement of lignite by such moderate heating.

Working in the other direction with a view to increasing the tar products, F. Fischer and H. Schrader[20] heated a lignite, which only gave 7% of tar (on ash-free fuel) at 400° C., with four times its weight of sodium formate and obtained over 23% of tar. Using an autoclave, under pressure from the steam and gases formed, twice the weight of sodium formate gave 43% of tar, whilst eight times the weight gave 48%. 400° C. was found to be the best temperature.

PEAT.

The Irish Peat Enquiry Committee has issued a report, which relates to the winning of peat and various economic factors.[21] There has, however, been an important addition published which deals with the carbonisation of Irish peat in vertical retorts.[22] The peat was in block form, 10 inches long by 2 inches square, which could be cut and sawn like hard wood. The blocks were broken down before carbonising. Sufficient steam (about 6% by weight) was passed through the retorts to quench the coke before extraction. Eleven tons was carbonised in 18 hours at 1000° C. The gas yield was 14,900 cub. ft. per ton of peat, calorific value 325 B.Th.U. per cub. ft. (gross). The carbon dioxide content was very high, about

[17] *J.*, 1921, 225T.

[18] *J. Ind. Eng. Chem.*, 1921, **13**, 23.

[19] *Roy. Soc. Proc.*, 1921, **A99**, 236; *J.*, 1921, 499A.

[20] *Brennstoff-Chem.*, 1921, **2**, 161; *J.*, 1921, 457A.

[21] Fuel Research Board, H.M. Stationery Office; *J.*, 1921, 229A.

[22] *Fuel Res. Bd. Tech. Paper No.* 4; *J.*, 1921, 759A.

18%. At the lower temperature of 800°–900° C. over 12 tons was carbonised; the gas yield was 13,760 cub. ft. with a calorific value of 340 B.Th.U. The charcoal came out of the retorts in much the same form as that in which the peat was charged, but the volume was greatly reduced and the weight of carbonised product was about 27% on the peat charged.

This charcoal is stated to form an ideal fuel for suction gas producers, although the ash content was nearly 10%. It would be of interest to know how this would affect the working of such producers.

The general results obtained per ton of peat charged in the tests at the two temperatures are given in the table below:—

	At 1000° C.	At 800°–900° C.
Peat coke, cwt.	5·38	5·40
B.Th.U. per lb. (dry)	12,560	12,650
Gas, cub. ft. per ton	14,900	13,760
Tar, galls. (dry)	12·6	21·3
Refined spirit (galls.) ..	—	0·36
Oils (galls.)	7·8	15·1
Pitch (lb.)	43·4	53·7
Liquor, gallons	95·5	87·5
Ammonium sulphate (lb.)	29·2	24·8
Methyl alcohol (lb.)	1·53	1·44
Acetone (lb.)	—	1·14
Acetic acid (lb.)	8·35	7·49

A portion of the tar was steam distilled yielding the equivalent of 5·2 galls. of light spirit (sp. gr. 0·866) per 100 galls. of tar. By further refining and distilling to 170° C., purified spirit equivalent to 1·7 galls. per 100 galls. (0·36 gall. per ton of peat) was obtained. The remainder of the steam distillate gave a further 0·7 gall. (distilling to 210°) per 100 galls. of tar.

The retorts were heated by a portion of the peat gas, about one-third of the total being required in the high-temperature distillation, and it was estimated that with a throughput of 3 tons per retort per day the surplus gas per ton of peat would be nearly 8000 cub. ft

of 325 B.Th.U. Removal of the high carbon dioxide content would greatly improve the gas, although for internal combustion engines this might not be necessary.

Powdered Fuel.

The many advantages arising from the use of finely pulverised fuel have led to fairly extensive development of the system. Installations are becoming common in the United States, and the large electric generating station at Hammersmith is equipped for powdered coal,[23] the particular system adopted here being that of Holbeck. Briefly, the coal, after passing a magnetic separator, passes to a rotary dryer, where the moisture is reduced below 1%. After pulverising it is screened; for general purposes 85% passes a screen of 40,000 perforations per sq. inch, and 95% through 10,000 perforations. The pulverised and screened coal passes into an air separator, where the coarser particles drop out and the fine material is drawn by an exhauster fan to a main collector and finally into the main storage bin, where it is deposited and the air returns to the air separator. From the main bin the coal dust is carried by a screw conveyer to a fan and is sent forward through a main, with its primary air, to the burners. Any surplus is carried on through the main back to a second small hopper above the main bin, into which it ultimately falls. An automatic control determines that the amount of dust and primary air is proportional to the demands of the furnace. The velocity of the dust in the mains is about one mile per minute and the mixture is said to be so rich in coal dust as to be non-flammable. By the return system adopted, when the burners are shut down, all dust in the mains etc. quickly gets back to the main storage bin. With a Babcock and Wilcox marine-type boiler, 6994 sq. ft. of heating surface, 81% efficiency was obtained, the fuel being rough Yorkshire slack containing 22·15% ash.

H. Kreisinger and J. Blizard[24] point out that good results with powdered fuel are more a matter of proper furnace and burner design, and the way in which air is supplied, than of fineness of the dust. Good results are claimed for a much coarser grading than is usual, *e.g.*, 88·6–93·2% passing 100-mesh (per linear inch) and 64–74% passing 200-mesh. Boiler capacity is said to be largely dependent on the capacity of the combustion chamber, present experience showing that the best results are obtained by burning 1–1·5 lb. per cub. ft. per hour, although "good" results are obtained over the wider range 0·5 to 2 lb.

J. Anderson,[25] who is chief engineer to the Milwaukee Electric Railway and Lighting Co., and who has had a big experience with

[23] *Engineer*, 1921, **132**, 90.
[24] Amer. Soc. Eng., 1921.
[25] *Engineer*, 1921, 132, 169.

powdered fuel, deals at length with the advantages and plant. He considers that there is a minimum limit to the size of plant suitable for powdered fuel, viz. 2500 h.p. per 24 hours. Tests with five similar boilers with powdered fuel and mechanical stokers gave the actual gross efficiencies of 86·67% for powder, and 76·8% for stokers, but the net efficiencies were not greatly apart, viz. 72·32% and 70·88%. Considerable advantage, however, arises when the boilers have to be "banked"; with powdered fuel the brick-work is so hot that after dampers and air inlets are closed pressures can be maintained for several hours.

One of the difficulties which has been met with in the use of powdered fuel has been slagging of the ash, rendering its removal difficult. Anderson says that such trouble is due to insufficient air, so that furnace temperatures are too high. Properly operated, the ash should be deposited, and can be removed twice every 24 hours. A large proportion of the ash is carried away in the gases and out of the stack, and in the Milwaukee plant there has been no tendency for slag to form on the tubes.

According to a Melbourne correspondent[26] pulverised lignite is coming into use and several firms have adapted their boilers to it. Provision is being made for the installation of a large pulverising plant near Melbourne to supply the fuel to industrial undertakings. No mention is made about the conveyance of the fuel to the user, but the delivery of any form of pulverised fuel for comparatively short distances from the pulverising plant through mains by compressed air would appear quite feasible. The system would have to be provided with return mains in order to bring back the dust to the central plant when the outlying installations shut down, otherwise it would deposit in the mains.

"Smokeless Fuel."

In a paper on "Low-Temperature Carbonisation and its Application to High Oxygen Coals," S. W. Parr and T. E. Layng[27] put the case for low-temperature carbonisation thus: "If a Scotch oil shale, yielding 20–25 galls. of oil per ton and no by-products of value (sulphate of ammonia ?) is a workable proposition, why may we not look with favour upon a bituminous coal having a potential yield of liquid fuel of 20–30 galls. per ton and a by-product in the way of a smokeless solid fuel of even greater value than the oil ?" It seems to be assumed by these authors that the liquid products from coal are of equal value to those from shale. They point out that the problem is to get the heat to the centre of a poor conducting mass without doing violence to all ideas of temperature control, and point to the coke oven, where, with an 18-inch section and a wall temperature of 1000° C., the carbonisation stage at the centre

[26] *Times Eng. Supp.*, Dec., 1921, 336.

[27] *J. Ind. Eng. Chem.*, 1921, **13**, 14

requires at least 14 hours out of a total of 18 hours. Parr and Layng refer to, but give few useful particulars of, a suggested process of theirs which is dependent upon the "autogenous" exothermal reactions of coal decomposition, which are most in evidence between 300° and 400° C., and state that the volatile matter in the product is from 5 to 10%, depending on the coal and the ultimate temperature.

The difficulty of heat transmission sufficient to bring about the necessary carbonisation of the interior mass with moderate wall temperature, and in a reasonable time, may be regarded as solved in two or three modern systems, in which the charge is stationary. In the Smith plant, already operating on a fairly large scale in America, high wall temperatures are the practice and the coal is continually stirred during carbonisation, and passes continuously through the retorts, so that whilst the actual distillation takes place at a low temperature (465°–525° C.), the big temperature gradient ensures rapid heat penetration.

The Smith "continuous system" certainly marks a distinct advance in carbonisation, and excellent accounts of the plant have been given by C. H. Thurston [28] and H. A. Curtis.[29] A noteworthy point is the use of carborundum walls for the special heart-shaped section retorts. The volatile matter is reduced to about 10%; the resulting semi-coke is a soft porous material, suitable for water-gas plants, producers, and boiler firing, but is not adapted for transportation. It is ground and briquetted with hard pitch, and then retorted at 1000° C. in retorts set at a slope of 30°. The volatile matter is reduced to 3% and the blocks have proved very suitable for use under stationary, locomotive, and marine boilers, and are claimed to be suitable for blast furnace use. It is questionable, however, whether with so low a volatile content as 3% such fuel would be suited to the open fireplace in this country.

One advantage of such a process is that it can deal with a wide variety of bituminous coals; owing to the retorts being only half-full and the agitation of the charge, the troubles met with in several designs of plant owing to swelling of the charge and difficulties of discharging do not arise. Over one hundred coals have been tested with satisfactory results. The average results for twenty-nine coals containing over 32% of volatile matter were: briquettes, 66% (12,874 B.Th.U.); gas, 8457 cub. ft.; dry tar, 34 galls.; ammonium sulphate, 21 lb.; light oil from the gas, 1·87 galls. per ton dry coal.

An extensive low-temperature plant of the Tozer design is to be erected in South Africa,[30] and will consist of 24 Tozer retorts, with

[28] J., 1921, 51T.

[29] *J. Ind. Eng. Chem.*, 1921, **13**, 23.

[30] *Engineer*, 1921, **132**, 336.

a maximum capacity of 120 tons per day. After condensation, scrubbing, etc., the retort gas (about 4800 cub. ft. per ton) will be mixed with gas from the producer plant, a portion of the mixed gas being taken to the retort settings. Alternatively the low-temperature gas may be passed to the settings. Seven producers will gasify the low-temperature coke, there being provision for ammonia recovery and oil washing. The bulk of the mixed gases will generate steam in water-tube boilers, and this steam will drive two turbines, each 1250 kw. at 2000 volts. A calcium carbide factory with three single-phase 800 kw. furnaces will form part of the plant and is estimated to produce 4200 tons of carbide per annum.

Considerable publicity has been given to the new Barnsley plant of Low-Temperature Carbonisation, Ltd.[31] The technical difficulties due to swelling of charge and the difficulty of discharging have been overcome by the use of collapsible perforated plates (of manganese cast iron) so arranged in the flat retorts that when charged there is a layer of about three and a half inches of coal between either side of the plates and the retort wall. After carbonisation the plates are brought closer together, and at the same time given an upward and downward motion respectively, so relieving any pressure and breaking down adhesion of the coke. The fuel leaves the retorts in slabs about 3·5 inches thick and two or three feet across. One of the difficulties with low-temperature coke has been the quenching, for water caused a good deal of damage. In the Barnsley plant it is cooled in an air-tight chamber below each retort and each chamber is water-jacketed. According to *The Engineer* (*loc. cit.*), the product from the entire battery of retorts did not appear to be equally carbonised, "some of the pieces appeared to contain a percentage of more or less green coal which would certainly not be free from smoke."

The following results were obtained in a Tozer plant for a throughput of 22 tons of bituminous coal of the proximate composition: moisture, 2·34; volatile matter, 25·10; fixed carbon, 53·65; ash, 19·0%. The yields per ton were: smokeless fuel, 16 cwt. (moisture, 3·9; volatile matter, 9·85; fixed carbon, 63·11; ash, 23·34%); crude oil, 15·2 galls. (containing 17·4% of tar acids); motor spirit (by stripping), 2·5 galls.; ammonium sulphate, 36·8 lb. The smokeless fuel when gasified in a Moore producer plant gave 124,000 cub. ft. of gas per ton, equal to 99,200 cub. ft. per ton of coal retorted; and 106 lb. of ammonium sulphate (85 lb. per ton of coal charged). The retort gas would be about 5800 cub. ft. per ton.

The whole fraction of a Barnsley tar distilled up to 300° C. (about 57%) has been successfully used with a cold start in a

[31] *Engineering*, 1921, **112**, 596; *Engineer*, 1921, **132**, 464.

Ruston-Hornby oil-engine, the consumption at most economical load being 0·49 lb. per b.h.p. All low-temperature tar oils are characterised by a high percentage of tar acids—up to 30%. The oxygen content is consequently high and detracts from their calorific value. It is doubtful whether it would be economically sound to remove the acids, but from the point of view of the use of such products in Diesel-type engines the behaviour of the tar acids on combustion requires special investigation.

Oil Fuel.

Owing to the coal strike there was a remarkable increase in the use of fuel oil in this country, and many of those who adapted their plants for its use were so convinced of its advantages that serious consideration has been given to the advisability of continuing the use of oil. The economic question will naturally determine how far, and in what particular cases, it will pay to use oil instead of coal, and in this connexion it must be remembered that the total crude oil output of the world only amounts to 10% of the coal output, expressed in terms of relative calorific value. Further, ensured supplies and a steady price can alone determine the extended use of oil, even assuming the price enables oil to compete, all its advantages considered, with coal.

Although the coal strike commenced at the end of March, owing to stocks in hand and the time required for the conversion of plants from coal to oil, it was not until the beginning of May that a marked increase in the use of oil was found; by the end of May one large firm was supplying ten times the normal quantity; June was the record month, when some fifteen or sixteen times the normal deliveries of fuel oil were made, and the timely assistance oil gave enabled many plants to carry on which would have had to close down. A great increase at once arose in the use of oil for locomotives and in large electric power plants, and among industries vital to the country which carried on with the help of oil may be mentioned iron and steel, cotton mills, paper mills and glass works, besides the general use for manufacturers' power plants.

Supplies of oil appear to have been ample, but the greatest difficulty was experienced in providing transport, as the oil had to be distributed from a few centres, mostly on the coast. It was mostly conveyed by road tank wagons and by barges. Some was sent in barrels, indeed one firm filled and despatched in one week 12,000 barrels. Owing largely to high freights and the general delay of railway tank wagons, a comparatively small portion was conveyed by rail, possibly some 25%.

A type of oil fuel atomiser, the "Rotamisor," which introduces a novel method of spraying, has been brought out. The oil is fed through a central pipe to a cone with serrated edges. On this

pipe the cone rotates on ball bearings, being driven by vanes in the air or steam blast pipe in the larger atomisers; in the smaller sizes (0·5–1·5 galls. and 1–5 galls. per hour) the cone is rotated by an impulse-type turbine wheel, the rapid rotation forming a spray. It is claimed that atomisation is very perfect and the flame consequently not so intense as many oil flames, a "soft" heat resembling that of a gas-fired furnace being obtained.

R. E. Mathot[32] has contributed results of tests with vegetable oils in semi-Diesel type engines, mostly two-cycle, which he says, work perfectly with such oils. The oil consumption per b.h.p. averaged for palm oil, 0·69 lb.; cotton-seed oil, 0·65 lb.; and for a heavy mineral oil, 0·57 lb. He concludes that where the oil is used on the spot, and has not been subjected to costs for handling and transport, the cost per b.h.p. hour would be 0·8–1·0 pence.

The use of vegetable oils, Mathot says, may have an important bearing on transport in the producing countries, where the price of mineral oil is usually very high and it is practically unobtainable, except at certain centres. In particular he directs attention to castor oil, which he has burnt with success, at a consumption of 0·52 lb. per b.h.p. hour, and proceeds: "According to certain colonial authorities, the plant from which the oil is abstracted grows as a weed in almost all tropical and semi-tropical countries. If cultivated for the purpose it may become a valuable source of motive power in every colony." Perhaps here he has more particularly Belgian colonies under consideration.

Colloidal Fuel.

This development has attracted considerable attention since it was first mentioned in these Reports,[33] and a long and exhaustive paper by S. E. Sheppard[34] has appeared. L. W. Bates and H. O'Neill also visited this country and read two papers before the Institution of Petroleum Technologists.

Sheppard states that the idea of burning a suspension of carbonaceous matter in mineral oil appears to be nearly as old as the use of fuel oil. He might have added that horizontal-retort tar is not a novelty as a fuel, and contains anything up to 20% of "free carbon," held in more permanent suspension probably than the powdered coal in most "colloidal fuel," and that it is a "colloidal fuel" which has not been regarded with favour. With a view to meeting the great difficulty of supply of fuel oil, threatened by the German submarine warfare, Sheppard prepared "composites," which contained up to 30% of powdered coal incorporated with

[32] *Engineer*, 1921, **132**, 138.
[33] *Ann. Repts.*, 1919, 21, and 1920, 30, 81, 82.
[34] *J. Ind. Eng. Chem.*, 1921, **13**, 37; *J.*, 1921, 110A.

"an ancient specimen of oil from a laboratory oil bath—plus one or two things thrown in for luck," and the promise which these rough mixtures gave of stability led to the results being referred to L. W. Bates, Engineering Chairman of the Submarine Defense Association (U. S.).

Sheppard defines "colloidally combining" as "stably dispersing pulverised coal in fuel oil, forming a uniform composite, the stability of which at ordinary temperatures should be reckoned in months, while amply sufficient at higher temperatures to permit atomisation by fuel oil burners."

It is a very debatable point how nearly these composites approach the colloidal state, or if they are merely fine suspensions in fairly viscous media, with consequently a slow but nevertheless certainty of more or less deposition of the coarser particles in time. Stabilisers or fixateurs, such as lime soaps, which form emulsoid colloids with mineral oils, are added to prevent clotting and separation. These increase the viscosity of the oil, but this is not the sole condition conferring stability of suspension, for oils thickened by other means, *e.g.*, vaseline, to the same viscosity, gave much lower stabilities.

Further, stability may be obtained by peptising; thus tar oils containing creosote and naphthalene were found to stabilise the "free carbon" suspension in some residual oils from petroleum distillation. Sheppard found that composites to which peptising substances were added when maintained at relatively high temperatures increased in viscosity, the number of ultramicroscopic particles (in xylene solution) being greatly increased and showing the Brownian movement.

Peptisation does not appear to produce complete stability in the oil-tar medium. "Generally it is easy to secure 3 to 4 weeks' homogeneity. After this the composite generally separates into an oily supernatant top layer over a more viscous mass." It may be re-mixed "and only very slowly, tends to pass to a dense solid mass." The colloidal fuels of this type are claimed to be more readily and cheaply compounded than those in which stabilisation is effected by an external protective colloid—the fixateur—and are perfectly satisfactory as liquid fuels for land installations. Or, again, the two processes may be combined.

One of the greatest claims put forward for the value of colloidal fuel is its suitability for use on board ship. On shore there seems little ground for doubting its applicability, because stirring devices can easily be arranged in tanks, but on the other hand, what advantages does it offer in land installations over pulverised coal alone, or pulverised coal burnt simultaneously, but independently, with fuel oil? Until it can be very conclusively established that colloidal fuel will not deposit heavy sediments of the coarser coal particles,

allowing that the finer material remains indefinitely suspended, and that the accidental contamination with sea-water will not cause flocculation, no marine engineer will be likely to entertain the proposition of filling his oil bunkers, particularly double-bottoms, with a fuel which may cause endless trouble with blocked suction pipes. He has even had cause for tears with some fuel oils not intentionally containing "colloidal" carbon.

Most of the claims for the advantages of colloidal fuel may be conceded, such as that the ordinary methods of burning with fuel oil may be adopted (many engineers, however, expect considerable abrasion of the orifices of the atomisers); that per unit volume it may contain a greater number of heat units than oil alone; that it is free from risks of spontaneous combustion (but for all practical purposes so are coal and oil in bunkers); that a fire can be readily extinguished by water because the composite is heavier than water. The crux is stability. Sheppard expresses the belief that colloidal fuels can be made just as stable as needed, and that laboratory prepared samples have lasted 12–18 months, but he mentions in the succeeding paragraph of his excellent paper that "re-agitation, before sedimentation has proceeded too far, will give a further extension of life."

Petrol Engines.

A most important series of articles on the influence of various fuels on the performance of internal-combustion engines has been published by H. R. Ricardo,[35] and a comprehensive study of the various fuels, and the phenomena attending the combustion of those used by Ricardo, has been made by H. T. Tizard and D. R. Pye.[36] The investigations were generously financed by one of the large petroleum companies, who desired the work to yield results of real scientific interest, and not to be restricted to limits which would be of direct commercial value to themselves alone, and who generously gave permission for the publication of the results.

Two most important factors are liability to detonation and to pre-ignition; they are not the same thing—the former is the result of combustion, whilst pre-ignition is a cause of combustion. Carbon bisulphide has a very low ignition temperature (275° C., by adiabatic compression). Ricardo found that it could not be used in either of his experimental engines because of pre-ignition, but this was not accompanied by detonation—indeed, it actually raised the detonating point of the aromatic-free petrol used in the experiments, which had an adiabatic-compression ignition temperature of 353° C.

Ricardo has proved that the tendency of a fuel to detonate is so important that all other considerations are secondary, since the

[35] *Auto Eng.*, Feb.-Aug., 1921.

[36] *Loc. cit.*

compression ratio which can safely be employed is limited by the tendency to detonation, and the power output and efficiency are in turn dependent on compression ratio.

Whilst pressure is the paramount factor in determining detonation, other factors play an important part, namely the design of the combustion chamber, and turbulence (speed largely determines the degree). The rate of burning of the mixture is also important—a weak mixture and a richer mixture both slowing down the rate, but with the former there is too little range, whilst stronger mixtures, which give the necessary flexibility, enhance consumption of fuel. Continued detonation, which is evidenced by the blow on the walls of the cylinder producing audible "pinking," may induce pre-ignition because of the heating up of the plugs, or any projections in the cylinder.

But to the chemist the influence of composition is of paramount interest. Ethyl alcohol, acetone, toluene, and xylene could not be induced to detonate in the engines, and the addition of, for example, toluene would raise the detonation point *pro rata* with the weight added. Benzene proved markedly inferior to toluene in checking detonation, whilst xylene occupied a position intermediate between the two. Ethyl alcohol proved by far the most effective.

It was found that some fuels, notably benzene, gave pre-ignition when the compression was raised to a 7 : 1 ratio, without preliminary detonation, but the addition of a small portion of paraffins, naphthenes, methyl alcohol, and methylated spirits would induce detonation at high compression ratios.

The members of the same series of hydrocarbons may have widely varying effects on detonation. Thus it was found that a nearly pure heptane gave detonation with the low compression ratio of 3·75 : 1, whilst an aromatic-free petrol, of which heptane forms part of the lighter constituents, had a much higher ratio (4·85 : 1) and even in small quantities increased the tendency of hexane to detonate. It is concluded that the heavier members of the paraffin series detonate more readily than the lighter ones.

An interesting point is whether any connexion exists between detonation point and the spontaneous ignition temperature of the fuel. Broadly, the results showed that the latter might be taken as a very approximate indication of the tendency to detonate, but the relationship was unreliable. It does not appear from Ricardo's results that the vapour in the cylinder has an ignition point directly related to that of the liquid, as determined by the usual method of dropping the liquid into a heated vessel. Thus Ricardo found the self-ignition temperature of benzene by adiabatic compression with air to be 419° C., whilst Moore[37] gave 566° in oxygen by the drop method; for toluene the figures were respectively

[37] *J.*, 1917, 109.

422° and 516° C. Ethyl alcohol, again, gives practically the same "Moore" figure, 518°, as toluene, but a value nearly one hundred degrees higher (514°) by adiabatic compression than toluene.

Generally, the practical outcome of Ricardo's work, as far as composition of the fuel is concerned, is that if a sufficient proportion of aromatic hydrocarbons, particularly toluol, is present the majority of engines can be run at maximum efficiency on an economical mixture. But some engines are so badly designed from the point of view of detonation that they can only be run at the ordinary efficient compressions with an over-rich mixture, and this probably accounts in some part for the excessive petrol consumptions in the U. S. Bureau of Mines' tests referred to later (p. 30).

Appreciation of the importance of aromatic hydrocarbons is leading to vendors paying special attention to the composition of their motor spirit, and in this connexion the valuable method of estimating the aromatic content of petrol described by H. T. Tizard and A. G. Marshall[38] may be referred to.

Ease of starting with a petrol type engine depends upon a number of factors in the general design of the engine, particularly in that of the carburretter, but the vapour pressure of the fuel has an important and well-recognised influence.

With a cold engine the latent heat of vaporisation of a fuel becomes important, in conjunction with the fuel-air ratio by weight. For the usual fuels, petrol and benzol, these are practically the same, but with some other fuels, notably alcohols, they are very different. Thus the latent heat of vaporisation of alcohol is 2·5 times that of petrol, and about 1·6 times the weight of alcohol is required to give an inflammable mixture for a given cylinder volume. It follows that about 4 times the amount of heat is required to furnish a combustible mixture with alcohol than with petrol. For the practical use of alcohol the addition of a proportion of ether, with its high vapour pressure, is required to render starting easy. This type of fuel mixture is used fairly widely in South Africa under the name of Natalite.

The following conclusions respecting starting are set forth:—(A) On no petrol will an engine start from cold with an economical mixture strength. (B) On commercial petrol of reasonable quality a cold start can always be made provided sufficient fuel is admitted.

Much of Ricardo's work in this connexion is of primary importance in the design of carburretters, but his results also point to another cause of the very inefficient results recorded by the U. S. Bureau of Mines' tests (p. 30), where the carburetters were undoubtedly adjusted to ensure an easy start and flexibility, but allowing an unduly rich mixture to enter the cylinders in ordinary running.

[38] *J.*, 1921, 20T.

A comprehensive paper giving a comparison of an alcohol-petrol aviation fuel with aviation petrol has been issued by the U.S. National Advisory Committee for Aeronautics.[39] The work was carried out by V. R. Gage, S. W. Sparrow, and D. R. Harper. Aviation "alcogas" is stated to be "probably" a blend of 40% alcohol, 35% petrol, 17% benzol, 8% toluol, ether, etc. The characteristic of fuel mixtures of this type is their ability to work to high compressions without "knock." Two series of tests were made, one with a compression ratio of 5·6 : 1 (usual for petrol in the engines) and another at 7·2 : 1 ratio, which could not be used for petrol. At the low compression the mixture gave the same power as petrol at ground level, but at the equivalent altitude of 6400 feet about 6% more power; at the higher compression there was an average and fairly uniform increase of 4% at altitude. A fuel consumption per B.H.P. of from 10 to 15% more by weight was required as compared with petrol to secure this maximum power, but since the mixture was denser than petrol the fuel consumption by volume per h.p. was practically the same. The thermal efficiency of the mixture was about 15% higher than with petrol. Since unit weight of the mixture is about 22% lower in calorific value than petrol it is evident that the available energy is more fully utilised than in the case of petrol. A motor fuel by the same makers as "alcogas" has the following composition:—Alcohol, 40–60%; benzol, 25–35%; petrol, 30–50%.[40]

An important paper by A. C. Fieldner, A. A. Straub, and G. W. Jones deals with gasoline losses due to incomplete combustion in motor vehicles.[41] The tests were really undertaken by the U.S. Bureau of Mines to investigate questions relating to the ventilation of the proposed tunnel under the Hudson, being thus specifically concerned with the composition of the exhaust gases, but they throw a great light upon the waste of petrol by the average vehicle. Over one hundred lorries and passenger cars were examined, under winter and summer conditions, on the level and up and down gradients. The average percentage of carbon monoxide in the exhaust gases under all conditions of tests was:—for 5-seater cars, 6·3%; for 7-seater cars, 6·8%; for light lorries, 6·9%. These figures are closely approximate to the mixture composition required for maximum power, but are very wasteful from the standpoint of petrol consumption. An interesting test was one in which the mechanic set the carburetter according to experience at the "best" setting. The exhaust gases contained 10·2% of carbon dioxide and 6·4% of carbon monoxide. A further setting to give a less rich mixture gave 12% of carbon dioxide, 2% of carbon monoxide,

[39] *Rept. No.* 89.
[40] E.P. 128,917; *J.*, 1920, 715A.
[41] *J. Ind. Eng. Chem.*, 1921, **13**, 51; *J.*, 1921, 111A.

and a 31% increase in mileage! The theoretical air required per lb. of petrol for complete combustion is approximately 15 lb.; for maximum thermal efficiency about [illegible] lb.; for maximum power about 12–13 lb. It was concluded from the tests that 50–75% of the daily waste of petrol could be prevented by proper adjustment of existing carburetters. Higher percentages of carbon monoxide were found in the summer tests, the mixture being naturally richer than under winter conditions, which suggests the desirability of alteration in the setting of the carburetter to suit seasonal temperatures.

Some interesting particulars of tests of a marine Still oil engine[42] have been published.[43] It will be remembered that in this engine power is obtained from oil (on the Diesel principle) and steam generated by the otherwise waste heat in the exhaust gases from the oil cylinder and the cooling water jacketing this cylinder. Once the engine is hot no steam boiler is required, but for starting up one is employed. The particular engine referred to worked on the two-cycle principle, the cylinder diameter was 22 inches, the stroke 36 inches, and the following results were obtained:—

	10% over load.	Full load.	Half load.	Quarter load.
Engine b.h.p.	384	343	174	88·5
Oil per b.h.p. hour (lb.)* ..	0·382	0·360	0·367	0·415
Per cent. efficiency* ..	37·0	39·4	38·5	34·0
" " net ..	35·5	37·7	35·8	30·0

* All auxiliaries except scavenger blower were separately driven.

The report of a deputation representing the French Government and commercial interests was that with a good Diesel 4-cycle engine the oil consumption would have been at least 10% higher, and with a 2-cycle engine 20% higher.

Fuel Economy.

Probably the most important development in connexion with fuel problems during 1921 has been the very wide discussion which has taken place before various institutions on the better employment of fuel. Doubtless the high price of all fuels has done more towards advancing the economical utilisation than all the exhortations of specialists during the past few years.

42 *Ann. Repts.*, 1919, 4, 19.
43 *Engineering*, 1921, 112, 334.

The summer meeting of the Institution of Mechanical Engineers took the form of an informal conference on "Means of Improving the Thermal Efficiency of Heat Power Plants."[44] In all, sixteen papers were presented and a comprehensive range of problems was discussed. The Institution of Civil Engineers held several conferences, amongst them an Engineering Conference, where discussions on the utilisation of waste heat and of exhaust steam took place. Further, a Fuel Economy Review was promoted by the Federation of British Industries. In the United States a valuable series of papers were presented before the Industrial and Engineering Chemistry Section of the American Chemical Society.[45] The various papers covered a wide range, including low temperature carbonisation, lignite carbonisation, by-product coking, sulphur distribution in coal, the sulphur content of coke; colloidal fuels, gasoline losses due to incomplete combustion, and general fuel conservation. Several of the papers have already been noted.

In a paper, "Fuel Conservation, Present and Future,"[46] H. C. Porter points out that many expedients for increasing efficiency involve large changes in existing plant and equipment, which take time and incur large capital expenditure, which financial conditions would make it difficult to provide under present economical conditions. It would appear sound policy to concentrate in the first place on raising the efficiency of existing plant and a better utilisation of waste heat. The low efficiency of the average steam plant has been amply demonstrated recently, largely through the publication of tests by D. Brownlie. Control of combustion is the present most practicable method of dealing with this inefficiency, and the improvement of ill-designed plant would naturally follow, when a standard of efficiency to which any plant might reasonably be expected to work had been established. The advantages to be gained by super-heat and feed-water heating are appreciated widely, but general industrial plants are not constructed on these lines.

The utilisation of waste heat from furnaces is another direction where great economy is possible. Flue gas temperatures from most industrial furnaces are very high and the waste heat boiler may effect great savings. It has been pointed out elsewhere that the hot gases from many industrial furnaces frequently carry off over 70% of the available heat units of the fuel, when regenerators are not fitted, and the following heat balance sheet for an open-hearth steel furnace has been quoted :—Heat used in furnace, 27%; radiation losses of furnace and regenerators, 29%; radiation from producers, 10%; losses in producer ashes, 3%; heat lost in flue

[44] *Proc. Inst. Mech. Eng.*, 1921, No. 6.
[45] *J. Ind. Eng. Chem.*, 1921, **13**, 14—58.
[46] *J. Ind. Eng. Chem.*, 1921, **13**, 47.

gases, 31%. With a waste-heat boiler, 80% efficiency, and coal of 13,000 B.Th.U., the waste-heat boiler would utilise 3200 B.Th.U., the equivalent of 2·8 lb. of steam at 120 lb. pressure, with cold feed. A 35-ton furnace with 3000 lb. of coal gasified per hour would thus give 8400 lb. of steam per hour.

Porter considers that among the major improvements where the greatest economy is possible would be electrification of railways. Not only do locomotives burn coal very inefficiently when running, but standing with steam up, often at unnecessarily high pressure, entails waste. When the haulage and distribution expenses attached to coal are considered, and the freeing of trucks for other and remunerative merchandise, and further, the relief of the lines from coal haulage for this particular purpose, the advantages of electric drive from central stations are obvious. In the United States it has been estimated that a saving of 122,500,000 tons of coal per annum—two-thirds of the present railway consumption—would be effected. On the Chicago, Milwaukee, and St. Paul Railway, R. Beeuwkes states[47] that for train locomotive power a saving of 53% over locomotive fuel used has been attained.

The financial considerations involved in a general conversion of railways to electric traction are great and under present conditions probably preclude any great extensions, but already sections of the older railways are electrically operated, and proposals for extension are under consideration.

Centralised power development must also be largely affected by finance; the advantages are admittedly great from the fuel economy point, approximately 2 lb. of coal being consumed per kw.-hour at the switchboard, but the whole question has been so ably and exhaustively dealt with in the Report of the Nitrogen Products Committee[48] that further reference is unnecessary.

G. E. Stewart[49] discusses the utilisation of waste heat in gas works. He estimates that of the 300 therms in a ton of coal carbonised, about 22 % is not accounted for in the products, being either used in the process or wasted. The greatest loss is in the flue gases from the retort setting recuperators, the temperature of which may be 1000°–1250° F. Combustion may here be regarded as complete, but with an initial temperature of 1200° F., a waste-heat boiler working at 100 lb. pressure and with 70% efficiency would generate 1·56 lb. of steam per lb. of fuel. Even a better boiler efficiency might, however, be attained with the most recent forms using a fan suction.

Stewart gives examples of economies already effected. On inclined retort settings at Brentford nearly 970 lb. of steam is

[47] See Porter, *loc. cit.*

[48] *Cmd.* 482, 1920; *J.*, 1920, 25R.

[49] Inst. Civil Eng. Conf.: see *Engineering*, 1921, **112**, 77.

being raised per ton of coal carbonised; with Glover-West settings at Macclesfield, 700 lb.; on Woodhall-Duckham settings at Birmingham, 500 lb. Of course the efficiency of steam production (waste-heat boiler efficiency being the same) is inversely to the efficiency of regeneration.

With water-gas plants on fuel charged to the therm value of 100, Stewart estimates 10·3 therms lost in the sensible heat of the blast gases, 6·1 therms in the sensible heat of the water-gas. As the plants require steam the obvious advantages of utilising the waste heat in suitable boilers are evident. In producing blue water-gas all the issuing gases can be passed through boilers, but with carburetted water gas the tarry vapours in the "make" gas are unsuitable because of tar deposition. The use of waste-heat boilers with water-gas plants is becoming standard practice in the United States and this country.

At the same conference E. R. Dolby[50] dealt with exhaust steam and its employment for power and heating. In non-condensing engines 90% of the heat in the steam entering is discharged in the exhaust; in condensing engines or turbines 60% of the total heat of the fuel burned passes to waste with the cooling water from condensers. In Berlin all the hot water for some public baths is obtained from a public electric generating station three-quarters of a mile away, and public buildings on the route are also heated by water from the mains. Several instances were mentioned in the discussion of the saving of fuel by the utilisation of exhaust steam. One Metropolitan institution replaced hot-water boilers and reduced a coal consumption of 4000 tons to 3200 tons.

D. Wilson[51] in dealing with boiler-house management emphasised that inefficiency was mainly due to lack of scientific supervision, and that frequently common sense and a little engineering knowledge would effect improvement. In the discussion many instances were given of astonishing improvement when trained "combustion engineers" were employed. In one case eight Lancashire boilers which had been required for years were put under skilled management, and in three months it was possible to shut down three and yet give the works more steam than it had ever had before. The view was general that for all large steam plants the appointment of a specialist at a good salary would pay firms, but one speaker pertinently enquired where combustion engineers could be obtained. In some Engineering Colleges and Universities special instruction in the principles of combustion is given, but a real difficulty is for the students to obtain actual boiler control experience. Perhaps something could be done if College boiler plants (where installed) or heating plants could be put in the charge of the post-graduate

[50] See *Engineering*, 1921, **112**, 74.
[51] *Proc. Inst. Mech. Eng.*, 1921, No. 6.

pupils, but means must be found to provide industry with the scientifically-trained and practically experienced man when he is called for.

A useful graphical method by which it is possible to calculate the heat losses, excess air, and flame temperature from the data obtained from the analysis of flue gases, has been published by G. B. Howarth,[52] and F. Schulte[53] has also devised a graphical method using triangular co-ordinates, but the method is not as simple as Howarth's.

Miscellaneous.

W. Schwier[54] dealt in a series of papers with the important question of fuels for metallurgical furnaces, pointing out that calorific value alone is not a satisfactory basis of value, because flame temperature is one of the most important factors and calorific value is no criterion of this. Schwier reommends a valuation figure which is the product of the net calorific value and the theoretical flame temperature, multiplied by 10^{-6}. Calculated flame temperatures may be open to criticism, but with the same data the results are doubtless fairly relative, and so Schwier's formula would hold. Other important points which he considers are the effect of moisture, which lowers flame temperature considerably, but is not usually accounted for in gaseous fuel analyses, and the influence of other gases accompanying a particular gas or gases in a gaseous fuel. Thus he considers that the utility of carbon monoxide is different in water-gas and in producer-gas.

An interesting paper on power gas from sewage was presented by J. D. Watson before Section G, British Association, in September last.[55] The gas is the result of fermentation and analyses show a methane content of from 20 to 79%. A description was given of a small sludge pumping plant at Birmingham, designed to give 25 b.h.p. for a working period of six hours daily. The gas is generated in suitable closed tanks and, in the trials, contained 43% of methane. It was observed that after a certain stage of putrefactive decay was reached the sludge gave off no further fœtid odour. An ordinary type of gas-engine was employed; at 250 r.p.m. on town gas it developed 34 b.h.p. With the sludge gas the engine ran satisfactorily with 60–70 explosions per minute developing 17–18 b.h.p., from which it was concluded that the heat supplied in the fermentation gases was 1·8 therms per hour. The author says that Birmingham deals with 400,000 tons of wet sludge per annum, London with not less than 2,000,000 tons. On the basis that there

[52] *J.*, 1920, 329T.
[53] *Glückauf*, 1920, **56**, 532, 536; *J.*, 1920, 812A.
[54] *Stahl u. Eisen*, 1920, **40**, 1033, 1108, 1170, 1236; *J.*, 1920, 713A.
[55] See *Engineering*, 1921, **112**, 456.; *J.*, 1921, 748A.

are 9000 tons of dry solid in the Birmingham sludge; this would generate 320 million cub. ft. gas, which at 20 cub. ft. per b.h.p. hour, would be equal to 16 million b.h.p. hours, or 4400 h.p. per day of 10 hrs.

Reference has been made in a previous Report[56], to the D. J. Smith gas producers and their use for mechanically-propelled vehicles. This has been extended to their use for small boats etc., with very successful results. In tests made under Admiralty supervision in a 35-foot boat fitted with a 70 h.p. 6-cylinder Brooke petrol engine, the producer had a 14-inch diameter grate and the weight of the complete plant was 3·5 cwt. The fuel supply and the removal of ash were controlled by feed and cam shafts driven by the engine but at greatly reduced speeds, so that operation was automatic. The special feature of the plant which renders it suitable for use in boats is the small amount of cleansing which the gas requires, owing to the continuous fuel feed and the working down of the raw fuel at once into the incandescent fuel bed by the rocking grate bars. It was realised that the engine could not give the same power on producer-gas as on petrol, so consumption trials were carried out on petrol at various speeds, and then at approximately the same speeds on producer-gas. Some results at practically the same speed are summarised below :—

Fuel.	Average revs. per min.	Nautical miles run.	Speed, knots.	Fuel used per knot, lb.	Cost per knot, pence.
Petrol	656·5	14·7	7·65	3·76	20·75
Welsh anthracite ..	665·7	38·4	7·50	3·80	1·10
Irish " ..	647·8	25·1	7·40	4·78	1·38
Dumfries peat ..	667·4	23·7	7·43	7·30	0·62

The report says that these trials demonstrated an extraordinary economy for the plant, and that it can be run continuously and reliably at steady revolutions.

The two papers by N. E. Rambush[57] on thermal losses in the gas-producer process and on a laboratory distillation test for fuel to be used in gas-producers will repay detailed study.

Work has been continued on the propagation of flame[58] by W. R. Chapman,[59] who has investigated ethylene and propylene

[56] *Ann. Repts.*, 1920, **5**, 32.
[57] *J.*, 1921, 130T, 293T.
[58] See *Ann. Repts.*, 1920, **5**, 36.
[59] *Chem. Soc. Trans.*, 1921, **119**, 1677; *J.*, 1921, 835A.

mixtures with air. The lower combustible limits for ethylene are 3·4% (horizontal tube), 3·6% (vertical tube, downwards), and 3·3% (vertical tube, upwards), whilst the upper limits are respectively 14·1, 13·7, and 25·6%. With propylene the lower and upper limits in a horizontal tube are 2·6 and 7·4%. The maximum speed of propagation in a 2·5-cm. diameter tube was 142 cm. per second for ethylene. The maximum speed was not attained with a mixture containing the theoretical percentage of ethylene (6·5%), but with richer mixtures containing 7–7·25%. J. D. Morgan and R. V. Wheeler[60] have made further studies of the phenomena of the ignition of gaseous mixtures by induction coil sparks.

[60] *Chem. Soc. Trans.*, 1921, **119**, 239; *J.*, 1921; 335A.

GAS—DESTRUCTIVE DISTILLATION—TAR PRODUCTS.

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It is difficult to review the progress made in the year under review with any feelings of satisfaction. The financial position of the carbonising industries, maintained in such a flourishing condition in the previous year by the phenomenal prices obtained for coke and by-products, suffered almost complete collapse in the first few months of the year. Large stocks of coke were still in hand owing to disturbed labour conditions, and heavy depreciation had to be faced. Policy, often enough, became one of cutting down expenditure regardless even of economy. A lengthy coal strike before the situation was stabilised gave rise to a situation in which development became relegated to the background. Fortunately a relative improvement in prices for coke enabled the gas industry to recover much of the loss entailed in gas supply during the strike. The year thus presents a series of rapidly alternating conditions in which the various methods of gas production showed very varying costs.

Town Gas.

The Gas Regulation Act, as judged by its first year's appearance, cannot be said to have impressed the consumer. Coming into operation at a time when it was necessary in most cases to impose heavy increases in the price of gas, it has been subjected to criticism which might largely have been avoided if the increases had been made and explained separately. The experience of having to make a calculation only to find that the account is higher than ever before can hardly be expected to convince the average man that the Act has been to his advantage. Yet advantages to the consumer must certainly follow the working of the Act, provided that continuous records of the pressure and calorific value of the gas supplied are made. Such will necessitate constant quality and pressure so that gas-consuming apparatus can be designed and regulated to maintain the maximum efficiency.

A large number of undertakings have already been granted orders under the Act, and the remainder must come under the Act within eighteen months from the end of the year. Most of the "declared" values have ranged between 450 B.Th.U. and 500 B.Th.U. per cub. ft. The standard prices, which vary in each case, were fixed by the Board of Trade on the pre-war cost of manufacture plus increases shown to have occurred since, and form the basis on which dividends are authorised. As the price charged per therm varies from the standard, so the maximum rate of dividend may increase or must be decreased.

A reduction of the quality of gas supply below 450 B.Th.U. has been advocated, notably by G. Helps, who proposes 300 B.Th.U. gas as giving the cheapest form of therm. While this may be so, the limit is placed at the present time by the question of distribution. In many cases, even in pre-war times when the gas supplied ranged between 550 and 600 B.Th.U. gross, many gas concerns were unable to increase the size of their mains sufficiently rapidly to keep pace with increasing consumption. To-day it may be taken that the greatest number of complaints received are due to an insufficient supply of gas.[1] It will be realised that the increased supply necessary to make up for a reduction in quality becomes a peculiarly serious matter. T. Goulden [2] gives an example. Gas is pumped from Beckton through two trunk mains 4 ft. in diameter. The maximum initial pressure is 54 inches w.g. If the calorific value of 485 B.Th.U. were replaced by a calorific value of 350 B.Th.U., 38½% more gas would have to be pumped, with consequent increase of nearly three-fold in the pressure. Alternatively a third trunk main would have to be laid. The extra cost is estimated at over 1d. per therm, which might be greater than the difference in the cost price per therm of the two gases. As a rule depreciation in calorific value is accompanied by an increase in the specific gravity of the gas. This requires compensation by an increase in pressure in direct proportion. High-pressure distribution may no doubt help matters in this respect, but even this has its limitations.[3] J. W. Wood considers that a reduction of 500 B.Th.U. to 400 B.Th.U. would necessitate an increase in pressure in the proportion of 16 to 25, and even so there would be trouble with back-firing due to excessive aeration with the apparatus at present in use.[4]

In the delivery of gas of uniform quality many difficulties are experienced. To avoid stoppage of gas supply in case of breakdown gas plant is constructed in many units, and is almost always

[1] J. W. M'Lusky, *Gas J.*, 1921, **155**, 658.
[2] *Gas J.*, 1921, **154**, 536.
[3] B. R. Parkinson, *Gas J.*, 1921, **153**, 156.
Gas J., 1921, **153**, 96.

supplemented by water-gas plant or other special apparatus which is intended to meet sudden variations in consumption. For this reason large concerns are faced with the problem of adequately mixing large volumes of gases of varying nature. In very few cases, if at all, does the whole of the gas pass through one single distributing centre, and even in such a case no means have been taken for securing such mixing of different streams from different manufacturing plant. Where only one works is concerned, mixing may be accomplished largely in the holders, and an arrangement has been brought to aid in this.[5] It will be realised that gas concerns must often maintain a considerable margin over the declared value, which in effect becomes a minimum value and not an average.

The Committee set up in accordance with the Act to inquire as to whether it was desirable or necessary to impose any limitation on the amount of carbon monoxide supplied in town gas reported in the negative.[6] In their report the Committee traverse the changes that have taken place since the Water Gas Committee of 1898 reported on a similar matter and proposed a limit of 12% which, however, was not enforced. Since that time the fittings in use have very much improved in construction, and the present Committee were evidently much impressed by the considerable hygienic advantage which would follow the more general use of gas to the elimination of the domestic coal fire, as exemplified by the state of the atmosphere during the coal strike. Statistics of carbon monoxide poisoning were not entirely straightforward, and while the Committee was able to draw the conclusion that the water-gas supplied in town gas has influenced the death rate from "coal gas poisoning," the total death rate from this cause is so small (3·1 per million per annum, 1913—1919, England and Wales) that no serious effects are to be anticipated. The risk to general health from small escapes is considered to be negligible. The fact that during the coal strike the amounts of water gas, blue gas, and other gases containing very large amounts of carbon monoxide were distributed and used without any noticeable ill-effects, doubtless helped the Committee in coming to their conclusion.

The Committee, dealing with the subject of inerts, reported that it was not necessary or advisable to prescribe limits to the incombustibles in town gas at the present time owing to the fact that the gas industry is in a transitional period and should be left entirely free to evolve the most economical method of manufacturing gas.[7] It is suggested that a fresh inquiry should be held after

[5] C. C. Carpenter, E.P. 158,758; *Gas J.*, 1921, **153**, 812; *J.*, 1921, 208A.

[6] "Report of Board of Trade Committee on Carbon Monoxide," 1921; *Gas J.*, 1921, **155**, 429; *J.*, 1921, 332R.

[7] "Report of Board of Trade Committee on Gas Incombustibles," 1921; *Gas J.*, 1921, **155**, 484; *J.*, 1921, 353R.

three years have elapsed. Reference is made to the report of the Fuel Research Board in 1919, in which a limit of 12% was proposed. This limit was later modified by an agreement reached at a conference of representatives of the consumers, producers, and the Board of Trade to a limit of 20% for two years, 18% for the next two years, and 15% thereafter. Subsequently, owing to fresh experimental work it was thought advisable to have the inquiry, which has now delivered its verdict. From the evidence it appeared clear that for low-temperature work and for gas engines the effect of incombustibles in general in gas is negligible. As regards high temperature work the Committee did not consider that the evidence was sufficiently conclusive to warrant interference, especially as very often the effect of additional inerts was counterbalanced by an alteration in the composition of the other gaseous constituents.

Recording Instruments.

It is unfortunate that neither the Fuel Research Board nor the Gas Research Committee of the Institution of Gas Engineers has so far been able to recommend a recording calorimeter for official purposes. The trouble seems to be that no type of instrument can be relied upon to work accurately and automatically without any attention for more than a few days. Whether any recording instrument will ever do this seems doubtful.

The Simmance-Abady total heat recording calorimeter has been the object of study by both the Fuel Research Board[8] and the Research Sub-Committee of the Institution of Gas Engineers.[9] These investigations showed that the gravity governor automatically compensates in a satisfactory manner for changes in the specific gravity of the gas and for changes in atmospheric pressure and temperature when the specific gravity of the gas is within wide limits. A variation in the gas rate was found to be due to the choking of the burner. Dirty water gave a great deal of trouble owing to deposition of slime. No trouble was experienced with air locks, but changes in the viscosity of water with change of temperature produced a change in the water rate of about 0·7% per 1° C. change in temperature of the inlet water. In addition to spasmodic errors due to fouling of the burner and water pipes, variations of 10 units occurred which were traced to the effect of variations in the room temperature and inlet water temperature. Difficulty of variable humidity of the atmosphere was overcome. Radiation losses and gains amounted to 1·5 B.Th.U. per cub. ft. for each 1° F. difference between the mean temperature of the calorimeter body and its surroundings. The lag of the chart is 10–15 minutes. The record is finally considered reliable to about

[8] *Technical Paper No.* 2. T. Gray and A. Blackie, *J.*, 1921, 326A.
[9] *5th Report. Gas J.*, 1921, **154**, 677, 744 ; **155**, 35, 102 ; *J.*, 1921, 676A.

2% over 24 hours. Improvements have since been made. The Beasley instrument was also examined, and while it was found simple in construction and operation, free from troubles of water supply, and not subject to change of gas rate with variation in quality, it was found liable to change with alteration in atmospheric temperature and sensitive to draughts. Daily attention is necessary, and an accuracy of $\pm$ 10 B.Th.U. uncorrected for temperature and pressure should be obtained.

Recording calorimeters of other types are available and some are being examined. The Fairweather instrument[10] is again of the water flow type, and is based upon the Boys calorimeter, to which has been added a mechanism for giving a tabular number correction and a record. The former is obtained by the expansion or contraction of a certain volume of air sealed in oil and supporting a float. To the float is attached a tube which regulates the head of water supplied to the calorimeter. As the atmospheric conditions affect the enclosed air, so the float rises or falls producing a corresponding rise or fall in the head of water supplying the calorimeter. The gas is measured in a Parkinson escape-meter arranged so that the evaporation of water from the meter is largely avoided.

An electrically operated instrument, the Thomas calorimeter, has been working for some time at the Gas Light and Coke Co.'s Horseferry Road Station,[11] where it is said to have recorded within 1% from the daily average tests on gas from the same trunk main. Water flow is substituted by air flow in this instrument, and the temperatures are measured by electrical resistance thermometers. A small motor is necessary, and the instrument is somewhat elaborate, but the recorder may be placed some distance away and so can be installed at any convenient place.

Naturally the use of recording calorimeters for works' control has been widely extended, and in many cases one is placed on each gas stream. This involves the installation of an instrument for checking, unless such has been already incorporated in the recorder, when the expense is practically doubled. Calculation from gas analysis is not satisfactory, particularly when the proportion of blue gas etc. admixed is not known. Still-water calorimeters to which small samples can be brought can be used, but there seems to be a considerable opening for a convenient and accurate instrument for this purpose. The desirability of checking the quality of the gas at the suction side of the exhauster has led to the introduction of miniature exhausters which pull a stream of gas through a purifying train to recording instruments. Owing, however, to the lag of the instruments as well as of the small gas stream, the response is not immediate. Hence there is still a

[10] E.P. 162,826; *Gas J.*, 1921, **154**, 556, 628.

[11] *Gas J.*, 1921, **154**, 80.

tendency to employ jet photometers on the gas at the outlet of the works' exhausters. A more accurate instrument for this purpose is founded on the Brady indicator.[12] This instrument depends on the decrease in luminosity of a flame from a mixture of coal gas and air when the gas-air ratio is diminished. The point at which the luminous tip disappears provides an index of the heating value. This idea has been utilised in devising an instrument which is not intermittent and is largely automatic. In the "caloriscope" advantage is taken of the fact that the amount of air induced at a Bunsen burner is dependent upon the kinetic energy of the gas issuing from the jet, and this in its turn is dependent on the square root of the density of the gas, providing the pressure on the jet remains constant. As the rate of efflux of the gas varies inversely as the square root of the density, any alteration of the density is automatically corrected by a change in its inducing power. The apparatus consists of a Bunsen burner, provided with a good governor on the gas supply and a sensitive needle valve on the air inlet. The operation of the throttle is communicated to a pointer moving over a scale. By adjusting the valve to the neutral point of flame luminosity, the degree of throttling can be read off and provides an index of the calorific value. It is not recommended for other gases than straight coal gas,[13] but this difficulty may be overcome.[14]

A long-distance pressure register which is employed for immediately informing those in charge of "booster" plant of the pressure conditions in outlying districts is described by H. C. Widlake.[15] The gauge consists of a mercury cup carried on a float in a water cistern. Above the cup is fixed a circular frame containing pendant wires of varying length and resistance. As the pressure of the gas acts on the water seal the float rises, and successive contact is established with the wires. The instrument is placed in electric circuit with the works on telephone wires.

Combustion.

The combination of oxygen with hydrogen and hydrocarbons is of peculiar interest in the consideration of carbonising problems, particularly regarding partial and selective oxidation. H. B. Dixon originally showed[16] that water vapour was necessary for the combustion of carbon monoxide, and that this could be supplied by the combustion of any compounds containing hydrogen in the

[12] U.S.P. 1,370,948; E.P. 149,291; *J.*, 1921, 291A. See also *J.*, 1919, 938A.

[13] E. V. Evans, *Gas J.*, 1920, **152**, 511; *J.*, 1921, 3A. See also *Gas J.*, 1921, **153**, 165.

[14] W. M. Berry, *Gas J.*, 1921, **154**, 33.

[15] *Gas J.*, 1921, **154**, 376.

[16] *J. Chem. Soc.*, 1886, T. **49**, 94.

mixture. He showed that the reaction $CO + H_2O = CO_2 + H_2$ was reversible, and that if the carbon dioxide was removed, all the carbon monoxide could be oxidised by steam. Others have since regarded the formic acid which appears in this reaction and the hydrogen peroxide which is present in the combustion of hydrogen as intermediate products,[17] hence a series of reactions can be built up as follows:—

$$CO + H_2O = HCOOH. \quad HCOOH = CO_2 + H_2.$$
$$H_2 + O_2 = H_2O_2. \quad H_2O_2 = H_2O + O.$$

The combustion of methane can be similarly interpreted, the carbon oxidising to carbon monoxide and simultaneously the hydrogen oxidising to steam.[18] The decomposition of formic acid at 1150° C. is shown to give carbon dioxide and hydrogen, carbon monoxide being produced as a secondary product due to reduction of carbon dioxide by hydrogen.[19] It is also not without interest to find that benzaldehyde—an oxidation product of the higher ring compounds—gives, on pyrogenic decomposition, benzene and carbon monoxide with traces of anthracene.[20]

Heating, Lighting.

A most interesting lecture by R. V. Wheeler[21] illustrates the application of the study of combustion at Sheffield University. The maximum speed of propagation of flame of a given mixture of combustible gas and air is a measure of the tendency to back-fire. As the degree of primary aeration is increased so must the velocity of the gas-air mixture be increased by increasing the pressure. The "adjustability" of a gas depends on the range of gas-air mixtures lying between the mixture for complete combustion and that containing the largest proportion of gas which will propagate a flame at all. Assuming that the maximum speed of a current of gas-air mixture obtainable at the mouth of a burner is 50 cm. per sec., nearly the maximum degree of aeration could be obtained from methane and carbon monoxide without striking back, but with hydrogen hardly any at all. Methane would allow of a high primary aeration but still give a small range of adjustability. Carbon monoxide can give high primary range of aeration and the range of adjustability is large. Hydrogen would tend to strike back very badly. In mixtures the addition of methane to hydrogen reduces the speed of inflammability and a further addition of carbon monoxide increases it. Hence for burner work equal quantities

[17] H. Wartenburg and B. Sieg., *Ber.*, 1920, **53**, 2192; *J.*, 1921, 111A.

[18] *Cf.* Bone and Wheeler, *J. Chem. Soc.*, 1902, **81**, 535.

[19] J. A. Muller and E. Peytral, *Bull. Soc. Chim.*, 1921 (4), **29**, 34; *J.*, 1921, 162A.

[20] E. Peytral, *Bull. Soc. Chim.*, 1921 (4), **29**, 44; *J.*, 1921, 141A.

[21] *Gas J.*, 1921, **153**, 615; *J.*, 1921, 206A.

of these three gases would be most suitable. Mixtures of water-gas, coal-gas, and coke-oven gas should not give any difficulty in their utilisation. If any limit at all is placed on the composition of industrial gas it should be on the hydrogen. While the presence of incombustibles does not influence the calorific value of the gas-air mixture very much, the adjustability is very much reduced, and high inerts will mean that very slight variations in pressure would cause large fluctuation in the character of the flame and the distribution of heat throughout it; hence the heating of furnaces would tend to become inefficient.

The distribution of energy of combustion of a mixture of coal gas and air is dealt with by W. T. David,[22] who finds that at the moment of maximum temperature the distribution is: (1) internal thermal energy, 72–80%; (2) available chemical energy in unburnt coal gas, 10%; (3) heat loss to walls of reaction vessel, 10–18%, of total heat of combustion of the coal gas. C. M. Walter finds that for industrial furnace work of the type using atmospheric burners the results are affected by alteration in calorific value, a drop of 50 B.Th.U. having a marked effect.[23]

A very useful paper by W. Newton Booth on the possibilities of gaseous heating show the efficiencies that may be obtained with many types of furnaces, and the effect of the composition of the gas with regard to pre-heating on the temperature attainable. The rate of heat transfer is judged to be mainly one taking place by contact of the gaseous molecules with the surfaces to be heated. This is proportional to the difference in temperature between the gas and solid and to the "turbulence of flow" of the gas, *i.e.*, the back-pressure of the furnace. It has been calculated that if oxygen were available to support combustion in the incandescent burner the candle power would be as high as 250 candles from a Bijou mantle.[24]

A. Kling and D. Florentin find[25] that carbon monoxide is formed to a greater extent in inverted incandescent burners (0·29–1·23% of the gas consumed) than in upright burners (0·04–0·50%). The amount of carbon monoxide formed largely depends on the flame volume and the extent to which this is limited by the mantle. Gas burners should be constructed so as to avoid contact between the flame and colder bodies of large heat capacity.

Important work by E. Terres and H. Straube[26] emphasises the importance of primary aeration as affecting flame volume and the lighting efficiency. With upright burners the efficiency is reduced by admixture of other gases with straight coal gas. Carbon dioxide

[22] *Proc. Roy. Soc.*, 1920, **A**, **98**, 303; *J.*, 1921, 111A.

[23] *Gas J.*, 1921, **153**, 464.

[24] *Gas J.*, 1921, **153**, 223; **155**, 602.

[25] A. Kling and D. Florentin, *Chim. et Ind.*, 1921, **6**, 305; *J.*, 1921, 763A.

[26] *Gas u. Wasserfach*, 1921, **64**, 309, 329, 348, 440; *J.*, 1921, 461A, 502A.

is especially detrimental. Increased pressure forces the flame upwards and tends to fill the burner better giving increased brilliancy. Water-gas by shortening the flame causes a contraction away from the mantle. With the inverted burner the efficiency depends so largely on primary aeration that alteration in gas quality is of secondary importance. Dilution with water-gas with the same primary aeration increases the candle power. The lighting efficiency depends on combustion at the surface of the mantle—the extent to which it is completed there. The degree of secondary aeration also influences the efficiency. The secondary air diffuses inwards to a depth of 10 mm. inside the mantle. Combustion is complete 1 mm. outside the mantle. When primary aeration is complete secondary air dilutes and reduces the efficiency, hence there is a limit to primary aeration.

The report of the U.S. Bureau of Standards on the principles governing air injection is particularly interesting.[27] The conclusions reached are summarised as follows. (*a*) Where the gas rate is increased by change of pressure the momenta of the gas streams are proportional to the pressure. (*b*) Where the orifice is adjusted to give the same gas rate under the same orifice pressure with gases of different specific gravity the momenta of the gas streams are proportional to the square roots of their gravities. (*c*) The ratio between the momentum of the gas stream of the mixture is always the same for any one burner irrespective of orifice pressure, specific gravity of gas, or the volume of the mixture going through the burner. (*d*) When the pressure is changed to give the same gas rate for gases of different specific gravity the air entrainment is proportional to the gravity. (*e*) The pressure at any one point in the burner increases in direct proportion to the increase in the momentum of the stream of the mixture.

At the meeting of the International Commission on Photometry held in Paris certain definitions were agreed upon in respect to photometrical terms.[28] In regard to the lighting of factories rules were agreed upon pending further work being carried out. The minimum foot-candles recommended on the space or at the work to be illuminated varied from 5 for intricate work to 3 for office work, 2 for ordinary machining, and 1 for rough work, power plants, alleyways, and so on.

Public lighting, a subject which appears to have been neglected, receives attention from J. S. G. Thomas.[29]

Coal Testing.

The carbonising industries have always felt a considerable difficulty in valuing the coals used. Realisation of the variations of

[27] W. M. Berry and colleagues, *Gas J.*, 1921, **153**, 750.

[28] *Gas J.*, 1921, **156**, 229.

[29] *Gas J.*, 1921, **156**, 553.

different consignments of coal and the trouble that such leads to, together with the increase in the number of methods of treatment, has accentuated the difficulty. Many have placed reliance on testing plants from the size dealing with 1/1000 part of a ton to those of manufacturing size. But the results are rather a test of the capability of the person in charge of the plant than of the material dealt with. As a rule what is gained in accuracy by increasing the size of the plant is lost in time and cost. Probably the most satisfactory system is to test the individual characteristics of the coal by separate methods and finally summarise the results obtained. The results of tube distillation are often of considerable value in helping to form an opinion of the merits of coals. A method described by the Fuel Research Board[30] is likely to provide as useful information as any. The ingenious arrangement used for providing a steady pressure condition in the retort tube throughout the distillation and of collecting the gas evolved should be of service in many ways. A series of determinations on the same coal gave very concordant results and the method allows of the weights of coke, oils, liquor, and gas being obtained.

N. E. Rambush[31] gives an account of a method of fuel testing amounting to an estimation of the distillation products. In this case 2 kg. of coal is dealt with at a time, and a special arrangement for collecting tar and other products is described. A weight and thermal balance is finally drawn up.

In a method described by M. Dolch[32] the precaution is taken of sweeping air from the retort tube with dry nitrogen, but it is not advisable to dry the tar in a current of air as suggested.

Carbonisation.

The mechanism of carbonisation continues to receive attention. S. R. Illingworth, developing his theory of coking,[33] concludes that it is possible to produce any type of coking, steam, or anthracitic fuel by suitably treating a bituminous coal.[34] If the coking properties depend on the relative rates of decomposition and order of stability of the cellulosic and resinic constituents it should be possible to effect a preliminary decomposition of the cellulosic matter which interferes with the formation of the coke. S. W. Parr and T. E. Layng prefer to take the oxygen content as the criterion of the behaviour of coal. Coals which have a high oxygen content do not usually make good cokes owing to the phenol-soluble portion (the "binder") of the coal coming into contact with the oxygenated constituents and being adversely affected. If, however,

[30] *Technical Paper No. 1*, T. Gray and J. C. King, *J.*, 1921, 205A.
[31] *J.*, 1921, 293T.
[32] *Mitt. Inst. Kohlenvergasung*, 1921, **3**, 1 ; *J.*, 1921, 137A.
[33] *Ann. Repts.*, 1920, **5**, 51.
[34] E.P. 164,104 ; *J.*, 1921, 2A, 501A.

the coal with a high oxygen content is given a preliminary heating the oxygenated compounds may be destroyed and the resulting coke is improved.[35]

J. Roberts regards the more bituminous coals as containing an excess of "binder" which leads to expansion and porous coke. If this "binder" is diluted with non-coking material—breeze—a dense coke may be produced. Incidentally the breeze adds to the coal the property of quicker heat penetration. This method of treatment has particular reference to low-temperature work.[36]

Baille-Barrelle considers that Saare coals should be kept for some time at a temperature below 320° C. previous to coking at 750° C. in order to obtain good coke.[37]

Selective oxidation becomes particularly interesting if catalysis occurs during carbonisation as suggested by R. Lessing,[38] and this question will need examination in connexion with the proposal to use oxygen directly in internally-fired retorts.[39] While it has been generally understood that the admittance of air to fuel undergoing distillation is deleterious, it is interesting to find that the results of an actual experiment has been recorded by A. Thau,[40] in which oxygen was admitted to the top of a charge in a coke-oven. Except that the naphthalene increased at the expense of the benzene no bad effects were observed on the products by increasing the temperature of the arch until oxygen was admitted, when a rapid loss of ammonia was observed with increase in naphthalene and a thickening of the tar. Tar vapours readily absorb considerable amounts of oxygen. Hydrogen is eliminated as water and there is a considerable increase of the pitch content.[41]

In connexion with the proposals made by J. W. Cobb,[42] E. W. Jefferies gives a most interesting account of the possibilities raised if oxygen was available in large quantities and at a cheap rate. Taking the gasification of coal in a producer as an example, the steam-oxygen process would yield from a good gas coal of calorific value 14,240 B.Th.U. per lb., per 100 lb. of coal: gas 3100 cub. ft. at 0° C. of calorific value 400 B.Th.U., with about 5·7 lb. of condensable tar of doubtful value There would be required 30 lb. of dry steam and 640 cub. ft. of oxygen. The thermal efficiency would be 91·7% or 85·4% if the condensable tar is rejected. The composition of the gas is calculated to be as follows:—CO_2 3·0; C_2H_4 1·4; CH_4 7·6; H_2 28·0; CO 58·0; N_2 2·0%. Estimates based

[35] *J. Ind. Eng. Chem.*, 1921, **13**, 14.
[36] N.E. Inst. Min. Eng.; *J.*, 1921, 571A.
[37] *Comptes rend.*, 1921, **172**, 1580; *J.*, 1921, 500A.
[38] Inst. Min. Eng., 1921; see also *Gas J.*, 1914, **127**, 570.
[39] N. H. Humphreys, *Gas J.*, 1921, **156**, 39; see also *J.*, 1921, 307R.
[40] *Brennstoff-Chem.*, 1920, **1**, 52, 66; *J.*, 1921, 137A.
[41] L. Wallis. Private communication.
[42] *Ann. Repts.*, 1920, **5**, 48.

on present-day costs in America are given. The heat used in manufacturing the oxygen is reckoned not to exceed 85,000 B.Th.U. per 1000 cub. ft. of oxygen or 4·7% of the heat of the gas made.[43]

The work of J. Sinkinson[44] has been carried further by F. Fischer and G. Pfleiderer[45] who find that coal, peat, lignite, and wood all develop electrical conductivity at about the same temperature, *i.e.*, 700°–750° C. Up to 600° C. the residue from the carbonisation of these materials was always in the same condition as regards electrical conductivity. High- and low-temperature cokes can be distinguished by this means.

Direct determinations of the heat of carbonisation of coal have been made[46] and found to vary with the oxygen content of the coal. The heat supplied in the form of electrical energy was calculated from the current and voltage at the terminals of a quartz tube furnace which was placed in a bomb calorimeter filled with nitrogen. One gram of coal was used and a temperature of 700° C. maintained during the experiment.

A large amount of work has been done in attempting to obtain a quicker transference of heat to the charge in a retort than by the usual methods of heating flues. Some of the proposed methods will be referred to later. There is evidently scope in this direction, as the Fuel Research Board reports that no less than 60% of the heat required to carbonise one ton of coal is used to maintain the temperature of their vertical retort settings, *i.e.*, is lost by radiation and in the flue gases.[47]

G. Weyman, using apparatus and method previously described, shows that heat is much more readily transferred by the gas evolved in distillation than by conduction through the charges or by radiation. This method of heat transference is hindered or brought to a standstill by the formation of the plastic layer during the carbonisation of bituminous coals. Any factor, such as size of particles of the coal, presence of foreign matter, which influences the formation or continuity of the plastic layer, becomes of great importance to the rate at which coal may be carbonised. Coking coals which give thick, plastic layers are very difficult to deal with; gas coals with more volatile matter can be used more rapidly; while non-coking and anthracitic coals which do not give plastic layers can be carbonised with the greatest rapidity.[48]

The falling off in the gas rate shown by Weyman corresponds with the temperature of maximum plasticity of G. E. Foxwell,[49]

[43] *Gas J.*, 1921, **153**, 806; **154**, 374.
[44] *Ann. Repts.*, 1920, **5**, 39.
[45] *Chem. Zentr.*, 1921, **92**, II., 521; *J.*, 1921, 335A.
[46] *Brennstoff-Chem.*, 1921, **2**, 97; *J.*, 1921, 289A.
[47] "Report on Steaming in Vertical Retorts," 1921; *J.*, 1921, 333R.
[48] *J.*, 1921, 300T.
[49] *J.*, 1921, 193T.

who, in tracing the path of travel of gases in coke-ovens, has investigated the resistance to the passage of gas during carbonisation. The resistance reached a maximum at a temperature of 400° C. in the case of a Durham coal, at which point the coal was in a state of maximum plasticity. Non-coking coals show no appreciable resistance during coking and poor coking coals very little. The gas travels up the interior cool zone up to the time of the setting-up of the plastic layer and then for the most part travels through the coke. With wet coal very little, if any, of the steam evolved passes through the hot zone and can therefore play only an indirect part in conserving ammonia. Only about 1/20th of the gas is generated in the low-temperature zone and contains half the total free nitrogen, but only 7–8% of the total ammonia. Of the ammonia liberated in the cool zone 70% was found to be fixed.

The effect of atmosphere on the liberation of ammonia has been further studied by A. C. Monkhouse and J. W. Cobb.[50] Nitrogen was used as an inert gas, and the amounts of ammonia liberated when hydrogen and steam were passed successively over coke formed at different temperatures were compared with those formed when the heating was made in the inert gas. With coke formed at a temperature of 500° C. 9·2% of the nitrogen of the original coal was obtained as ammonia on heating in a current of nitrogen and 26·8% with hydrogen. With coke prepared at 800° C. and 1100° C. the ammonia recovered was negligible in an atmosphere of nitrogen and very little in hydrogen. When nitrogen, hydrogen, and steam were passed successively over the same coke (prepared at 500° C.) the nitrogen recovered as ammonia expressed as percentages on the original coal was :—Nitrogen stage, 7·9 ; hydrogen stage, 24·8 ; steam stage, 29·9 ; total, 62·1%. The residue was found to contain only ash. When steam was used directly after the coke had been heated in nitrogen the whole of the nitrogen of the coke was obtained as ammonia much more readily. It appears that in the presence of steam or hydrogen, or both, the dissociation of the ammonia liberated is very small, but in the presence of nitrogen only dissociation may be great if the concentration is high, although the temperature is comparatively low. Sulphur liberated as hydrogen sulphide was found to follow the same course as nitrogen liberated as ammonia, increasing in quantity by treatment with hydrogen and again by addition of steam. This last phenomena has also been noticed by A. R. Powell,[51] who proposes to reduce the sulphur content of coke by passing hydrogen over it. At 900° C., hydrogen in presence of coke containing 1·2% of sulphur established an equilibrium at a content

[50] *Gas J.*, 1921, **156**, 234 ; *J.*, 1921, 760A. *See also* A. J. Franks, *J.*, 1921, 111A.

[51] *J. Ind. Eng. Chem.*, 1921, **13**, 33 ; *J.*, 1921, 110A.

of 0·25 lb. of sulphur per million cub. ft. Powell finds that the principal reactions which occur in the carbonising of coal containing sulphur are: (A) Complete decomposition of pyrite to magnetic sulphide and hydrogen sulphide occurring at 300°–600° C.; (B) The reduction of sulphates to sulphides—complete at 600° C. (C) Decomposition of one-fourth to one-third of the organic sulphur to form hydrogen sulphide. This occurs mostly below 500° C. (D) Formation of volatile organic sulphur compounds (E) Disappearance of a portion of the magnetic sulphide—the sulphur apparently combining with carbon. This reaction occurs mostly above 500° C. In addition the organic sulphur changes in character between 400° and 500° C. No carbon bisulphide can be found in the primary distillation products but it is formed by the action of hydrogen sulphide on the coking mass. While coke ceases to give off hydrogen sulphide at 600° C. a further evolution commences at a higher temperature in presence of hydrogen.[52]

New Methods of Carbonisation.

Among new methods of carbonisation are several which take advantage of heat transference by gas. In one[53] waste or other gas is drawn through the charge. H. Nielson introduces an internally-heated rotary retort to be used with producer or water gas.[54] It is reckoned that about 23 B.Th.U. is available from each cub. ft. of the carrier gas for carbonising the coal, or about 34,000 cub. ft. would be required per ton. The total expenditure of heat would be about 6–7%. The process may either be used for low-temperature work or carried to complete gasification. Town gas (400 B.Th.U. per cub. ft.) or power gas for electrical generating purposes may be the products. In other cases the coal is to be carbonised in a powdered state.[55] Thus coal dust is carried upwards into an expanding chamber by a current of gas from a previous carbonisation. In this way the larger particles are given a longer time to carbonise. The coke dust may be subsequently removed in a cyclone extractor and then burnt in a current of gas under a furnace. K. M. Balley proposes[56] to suspend coal dust in a current of superheated steam and bring this into contact with hot surfaces at 1400°–1500° C. where complete gasification occurs

[52] *See also* H. F. Yancey and T. Fraser, *J. Ind. Eng. Chem.*, 1921, 13 35; *J.*, 1921, 110A. R. V. Wheeler, *Gas World*, 1921, Coking Sect. June 4, p. 13.

[53] W. E. Davies, E.P. 165,825; *J.*, 1921, 574A.

[54] *Gas J.*, 1921, 156, 368.

[55] Underfeed Stoker Co. and S. McEwen, E.P. 154,253, 154,458, 169,389 *J.*, 1921, 37A, 805A.

[56] *Chem.-Zeit.*, 1921, 45, 789; *J.*, 1921, 649A.

A gas-producer may be used to provide hot gas for carbonising fuel in another chamber.[57]

In a plant consisting of a water-gas generator below a vertical retort the heat is provided by the partial combustion of the gas on its way to the carbonising chamber to carbonise the coal, while the heat of the generator is maintained by a further partial combustion of the gas.[58] Many other patents have been taken out for complete or partial gasification by plant consisting of combinations of vertical retorts with gas-producers, water-gas generators,[59] etc. The blow gases may be used for raising steam, which is then supplied to the generator.[60] In another case the air is passed downwards through the generator in the reverse direction to the steam.[61]

G. W. Wallace has a vertical retort with the gas offtake consisting of a perforated pipe inserted from the base upwards to draw off the products downwards from the centre of the charge.[62]

F. H. Robinson's plant, in which the coke from horizontal retorts is pushed back into a water-gas generator, is further described.[63] On a test run 55,000 cub. ft. per ton of 344 B.Th.U. gas, 54,285 cub. ft. of 366 B.Th.U., and 70,715 cub. ft. of 321 B.Th.U. gas were obtained in different hourly periods. The coal contained 13·5% of ash. The tar contained no separable naphthalene, but a somewhat high pitch content of 68·8%.

H. Rule[64] finds that a Tully plant working on coke gave 50,500 cub. ft. of 297 B.Th.U. gas. With colliery belt pickings (ash 23–43%) the gas contained more carbon dioxide and the output of gas was reduced by nearly one-half, but 18,000–23,000 cub. ft. per ton was obtained of 305–315 B.Th.U. gas and 5 galls. of tar. There would seem to be a distinct future for such plant on low-class fuel, particularly if ammonia could be recovered.[65]

Further results on this plant are described by C. H. Chester.[66] It is interesting to note that trouble has been experienced in the fuel "sizing" itself on entrance to the retort, the large falling to the sides and the small going to the centre.[67]

[57] W. P. Perry, E.P. 167,822; *J.*, 1921, 686A. *See also* McLaurin, Nielson, *loc. cit.*

[58] A. Birkholz, E.P. 148,820; *Gas J.*, 1921, **156**, 447.

[59] *Cf.* R. and J. Dempster, E.P. 157,036; *J.*, 1921, 139A.

[60] G. Helps, E.P. 156,812 and 165,456; *J.*, 1921, 139A.

[61] Woodall, Duckham, & Jones, Ltd., E.P. 164,935, 164,949, and 165,616; *J.*, 1921, 572A.

[62] E.P. 129,997; *J.*, 1921, 5A.

[63] E.P. 168,535; *J.*, 1921, 727A; *Gas World*, 1921, **74**, 368; *J.*, 1921, 423A.

[64] *Gas J.*, 1921, **154**, 93.

[65] E.P. 168,482; *J.*, 1921, 727A.

[66] *Gas J.*, 1921, **154**, 323; *J.*, 1921, 458A.

[67] *Cf.* G. Weyman, *loc. cit.*, and E. Gillett, *Gas J.*, 1921, **156**, 563.

Low-Temperature Carbonisation.

The production of smokeless fuel in America is a somewhat different question to that in this country, as in the former case the fuel is required to replace anthracite in stoves, while in this country the object is to replace raw coal by a free-burning fuel in open grates. It is doubtful whether closed stoves will ever be popular in this country. The Smith process,[68] the object of which is to produce a comparatively hard fuel, consists in crushing and carbonising the coal in an inverted heart-shaped retort continuously stirred, in which it is advanced lengthwise through. At a temperature of 480°–500° C. the volatile matter is reduced to about 10% in two to three hours, and the semi-coal is then mixed with pitch and briquetted. The briquettes are carbonised in an inclined retort at about 1000°–1100° C. for six hours, when they contain about 3·8% of volatile matter and have a calorific value of about 12,870 B.Th.U. The yields of products are said to be as follows[69] :—

	Primary.	Secondary.	Final.
Briquettes	—	—	70% dry
Tar (30% tar acids), galls.	22·4	5·6	28
Sulphate, lb.	2·24	20	22·24
Gas, cub. ft.	5,600	4,480	10,080

The MacLaurin process[70] has also been the subject of further trial[71] and has given good results with low-grade fuels as a producer for power gas.

The Low Temperature Carbonisation, Ltd., are reconstructing their plant at Barnsley and introducing an improved form of retort.[72] The bituminous slack used, of which 70% is non-coking, is held in an overhead hopper by a coal valve over the charge. The charge is held in position by two collapsible perforated steel plates which can be keyed outwards to form a narrow passage 4 in. wide between the retort walls and the plates on each side. These plates are said to have withstood the heat conditions well for over three weeks. The gas generated passes through the perforations in the plates into the gas space between them. By allowing the plates to swing inwards the charge is loosened and dropped through a rotary door into a cooling chamber, where it cools in absence of air. The 10-cwt. charges are carbonised in 7 to 8 hours, and the yields per ton are said to be : Coalite 14 cwt., gas 6000 cub. ft

[68] *Ann. Repts.*, 1919, **4**, 46.

[69] H. A. Curtis, *J. Ind. Eng. Chem.*, 1921, **13**, 23, and C. H. Thurston, *J.*, 1921, 51T.

[70] *J.*, 1917, 620.

[71] *Iron and Coal Trades Review*, 1921, June 24, p. 848, and Nov. 11, p. 688.

[72] T. M. Davidson, *Gas J.*, 1921, **153**, 37 ; **156**, 308 ; *J.*, 1921, 536A.

of 700 B.Th.U., and oil 15 to 22 gallons. The amount of surplus gas is uncertain. An efficiency of over 82% is claimed and the coalite is said to contain 8–10% of volatile matter and only 5% of breeze.

N. Young[73] favours a rotating tubular retort with loose iron balls inside to keep the mass consolidated. Heating is effected internally by the passage of hot gas, or externally, or in both ways. A further modification provides for the heating of the coal in the internal drum by the combustion of solid or other fuel in an external shell. F. Fischer[74] has a similar rotating cylinder arranged horizontally with a roller inside. This process is intermittent.

The Fuel Research Board have been experimenting in the use of triangular moulds[75] which prevent frothing and give a consolidated semi-coke, while on the other hand J. R. Roberts[76] uses coke-breeze as a diluent with coals of a swelling character in order to absorb the excess "binder" and give a dense, hard semi-coke.

Peat, Lignite, etc.

Methods of carbonising peat, lignite, and brown coal are in many cases akin to low-temperature methods. In view of the shortage of coal much attention has recently been given to these fuels, especially abroad. The experiments carried out by E. Stansfield[77] in carbonising lignite were with the particular object of obtaining a residue suitable for briquetting. He finds that if the maximum calorific value of the residue is obtained by carbonising at about 600° C., the value of the by-products is small and the gas is barely sufficient to provide heat for the retorts or the pitch sufficient in quantity to provide binder. Coal-tar pitch was found to be the most suitable binder and 13 parts to 100 parts of the residue was required—almost double that required for anthracite.[78]

In the treatment of peat Muller [79] finds that the moisture must not exceed 25% or the ash 5% if carbonisation is desired, against the 33–40% of moisture considered possible for producer-gas practice.[80] Muller found that the yield of gas was 30% of not less than 4000 cals. per cub. m.; tar 5% and ammonia 0·25%. The retort temperature was 1100° C. and the time allowed 4 to 6 hours. The liquor was very dilute.

[73] E.P. 134,529; *J.*, 1921, 74A.

[74] E.P. 146,287; *Gas J.*, 1921, **155**, 664.

[75] *Gas J.*, 1921, **155**, 32.

[76] *Loc. cit.*

[77] *J. Ind. Eng. Chem.*, 1921, **13**, 17; *J.*, 1921, 111A.

[78] L. R. Thomson, *J.*, 1921, 225T.

[79] *J. Gasbeleucht*, 1920, **63**, 817; *J.*, 1921, 73A.

[80] P. F. Purcell, *Fuel Res. Board Spec. Rep. No.* 2; *see also* E. V. Moore. *J.*, 1921, 229T.

An interesting trial has been made by the Fuel Research Board.[81] Peat blocks with 20% of moisture were roughly broken in the usual coal breaker and carbonised at the rate of 3 tons per day per retort in the vertical retorts. Except for trouble with the large volume of gas to be dealt with and blockage with dust, the trial was successfully carried out. From each ton of peat there were obtained 14,900 cub. ft. of 325 B.Th.U. gas, 12·6 gallons of tar (setting point 40°C.), 95½ gallons of 3·6 oz. liquor, and 5·4 cwt. of charcoal. The tar contained considerable amounts of paraffin. The gas contained about 18% of carbon dioxide, had sp. gr. 0·757, and gave out a heavy sickly odour on combustion. The sulphate equivalent of the ammonia in the large bulk of liquor made was about 25 lb. per ton. The dry peat contained 1·51% of nitrogen —a somewhat low figure according to Purcell.[82] The peat charcoal was of much the same form as the peat entering the retort and had a calorific value of 12,650 B.Th.U. per lb. dry.

The process of L. Tissier for carbonising wood,[83] using the exhaust gases from gas engines, might be of use for dealing with peat. Tissier finds that the exhaust gases leaving at 400°–450° C. will carbonise the wood in 12–24 hours at 250°–350° C., and the resulting charcoal is of good quality.

It is not without interest to find that wood has been carbonised successfully and the gas used for town supply at Birmingham and Steyning when coal supplies were short.

Horizontal Retorts.

The interest of those concerned with horizontal retorts must have been greatly stimulated by the interesting account of G. M. Gill.[84] Practical results of which those in charge of such plants may well be jealous are evidently largely due to the very careful control of which the paper is evidence. It is pointed out that the chief item of the cost sheet in a horizontal retort house is the cost of the coal. Every precaution, therefore, should be taken to give the coal the best treatment, and to avoid waste. The installation of double-sided step-grate producers has given a grate area considerably above the usual figure of 1·35 sq. ft. per retort. Settings of ten retorts in 5 tiers are used and the disastrous effect of using refractory materials which give permanent contraction is shown. A feature of the retorts is the sloping mouthpiece which enables tar drip from the ascension pipes to fall back into the retort. An interesting experiment of building a setting up of a mixture of unburnt fireclay and grog was brought to a successful

[81] *Technical Paper No.* 4; *J.*, 1921, 759A.
[82] *Loc. cit.*
[83] *Chim. et Ind.*, 1921, 5, 136; *J.*, 1921, 252A.
[84] *Gas J.*, 1921, 156, 212; *J.*, 1921, 759A.

conclusion. Much attention is given to charging. The $10\frac{1}{2}$ cwt. charges are given 10 hours and occupy 65% of the retort space. Expansion takes up 8% and the free space then is 17%. A special drum on the Arrol-Foulis charging machine helps in obtaining even charges and great attention is given to reducing the charging time. As a consequence of this, it is possible with the provision of a retort house governor on each setting to work with dip pipes unsealed. The inerts only total 9%. For properly burning off the charge the following temperatures were found necessary in the combustion chambers corresponding to the weight of charge :—1270° C. for 12-hour charges, 1310° for 10-hour charges, and 1400° C. for 8-hour charges.

W. Newton Booth refers to the falling off in the gas yield with increase of age of the retorts. While retorts may look in good shape and condition after running for 2000 days, it may not pay to run for over 900 days owing to loss of gas and infiltration of producer and waste gas by the increasing porosity and number of cracks. The question of the design of recuperators is mentioned. While these often succeed in materially reducing the flue gas temperature they do not seem to add proportionately to the preheating of the secondary air.[85] Possibly the replacement of recuperators by waste heat boilers might secure a better efficiency.[86]

A setting has been designed[87] in which the seal in the hydraulic main is regulated by a pressure box through which the tar and liquor flow. The level of liquor in this box is considerably lower than the level of liquor in the hydraulic main and is maintained or varied by gas pressure, which is brought to bear upon its surface in the pressure box. The system thus forms an arrangement similar to a U-tube with the liquor on one side lower than the level on the other. The gas pressure of 12–18 in. required to cause this difference is obtained from a pipe line led, say, from the purifier inlet. By placing a pressure comptroller on this pipe the liquor level may be regulated as desired.

Some attention has been given to the subject of ascension pipe stoppages. There is no doubt that oxygen admitted inadvertently plays a most important part and, as a result, a high temperature is developed in the pipes. This mostly takes place when the amount of gas passing along the pipe has fallen off in quantity. Schnurr advocates a water-cooled ascension pipe.[88] Cooling by liquor circulation is effected in the Congdon system, where the retorts on each side of each setting are connected by short lengths into a vertical cast iron rectangular main down which

[85] William Young Mem. Lecture, *Gas J.*, 1921, **155**, 601.

[86] *See* E. G. Stewart, *Gas J.*, 1921, **154**, 734.

[87] A. Meade, E.P. 165,581 ; *J.*, 1921, 573A.

[88] *Gas J.*, 1921, **155**, 164.

liquor is passed. Pressure conditions in each retort are thus neutralised and a common vacuum is secured no matter at what stage of distillation the coal in any one retort may be. W. H Warren[89] describes the results obtained from an installation of a modified system.

It has also been found[90] that by cooling the gas between the retort and the hydraulic main in some way such as by spraying with liquor, an increase in the yield of tar may be obtained and 60% of the tar may be recovered in the hydraulic main.

L. Stock believes that a successful system has been evolved for steaming horizontal retorts and a special setting is described.[91] It includes a waste-heat boiler built into the setting which raises most of the steam required to furnish the extra water-gas. The steam is admitted at low pressure (0·3 atm.), and it is claimed that the steam reduces the tendency of the hot walls surrounding the free space to overheat the gas. Sufficient heat is imparted to the steam by this means to cause it to combine with flaky carbon in process of formation.

Vertical Retorts.

A high duty has been obtained from waste-heat boilers installed on vertical settings. Preferably these should be built into a setting arranged for the purpose.[92]

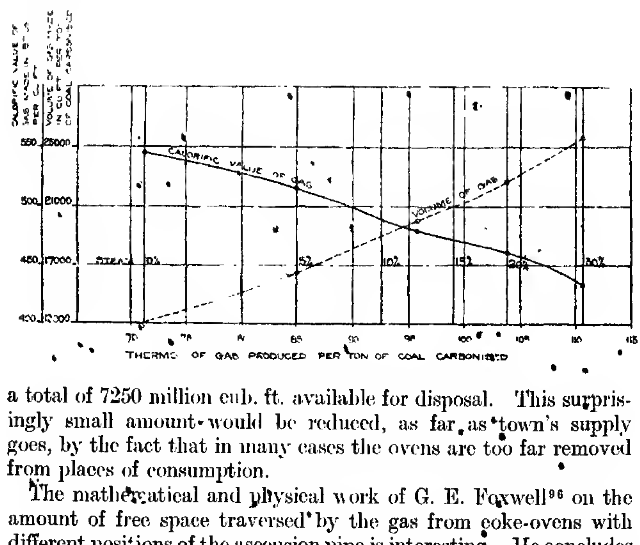
Steaming has been investigated by the Fuel Research Board.[93] Before trials of coals were commenced the heat losses from the setting of Glover-West retorts were determined. The heat required to keep the combustion flues at a temperature of 1260° C. when the retorts were full of coke was ascertained to be 12·4 therms per hour. This heat equivalent of the setting corresponds to 69·0% of the fuel used in the case of a Yorkshire coal at a throughput of 2½ tons of coal per day, per retort. With a combustion temperature of 1210° C. the expenditure was reduced to 9·6 therms per hour. Trials of three coals—a Durham, a South Yorkshire, and a Scottish coal—were carried out in such a manner as to compare as far as possible with the tests at Uddingstone.[94] The gas yields and the calorific value obtained in the test from the South Yorkshire coal are given on p. 58 in the curve taken from Fig. 3 of the Report. The temperature of the combustion chambers was 1260° C. and as much as 33% of the total heat of the coal was converted into gas of 460 B.Th.U. with extra amounts of tar and ammonia.

[89] *Gas J.*, 1921, **155**, 723.
[90] Binder, *Gas u. Wasserfach*, 1921, **64**, 129; *J.*, 1921, 335A.
[91] *Gas J.*, 1921, **153**, 804.
[92] S. Glover and J. West, E.P. 163,150; *J.*, 1921, 461A.
[93] *Report Fuel Research Board*, 1920; *J.*, 1921, 333R.
[94] *Ann. Repts.*, 1920, **5**, 44.

Generally speaking it is considered that it will be found economical to steam up to at least 20% of the weight of coal. While there are one or two points difficult to understand, such as the low yields of ammonia, the Report should be closely examined in the original by those interested.

Coke-Ovens.

As a result of a Board of Trade inquiry[95] it is fo
7275 by-product ovens (about 85% of those normally in operation) 3010 are regenerative. The gas yield averages about 10,000 cub. ft. per ton of 420–550 B.Th.U. gas. In those of the recuperative type 66–100% is used for heating the ovens while from the regenerative type 50–60% is used. A total of 37,250 million cub. ft. per annum is utilised in other ways than for heating the ovens, leaving



a total of 7250 million cub. ft. available for disposal. This surprisingly small amount would be reduced, as far as town's supply goes, by the fact that in many cases the ovens are too far removed from places of consumption.

The mathematical and physical work of G. E. Foxwell[96] on the amount of free space traversed by the gas from coke-ovens with different positions of the ascension pipe is interesting. He concludes that the gas has twice as far to travel when the ascension pipe is placed at the end of the oven chamber as it has when the pipe is placed in the centre, but that the time spent by the products in the oven is the same wherever the ascension pipe is placed. The mean velocity of the gases in the oven is one-half the velocity of the gases entering the ascension pipe. The author finally concludes

[95] *J.*, 1921, 256R.

[96] *Gas World*, 1921, *Coking Sect.*, Feb. 5, p. 12, and April 2, p. 11; *J.*, 1921, 193T.

that no disadvantage whatever is incurred by changing the position of the pipes. It is not certain, however, that the amount of decomposition of the gaseous products is solely dependent on the time during which they are in the free space, and it might conceivably be higher for an increased travel and proportionately increased velocity. T. Johnson[97] prefers a centrally-placed ascension pipe and suggests an oval cross-section as giving greater cleaning facilities. Some interesting curves are given showing the temperature at the top and bottom of ascension pipes at different carbonising times. During the greater part of the time a temperature of over 600° C. is experienced.

A patent has been taken out for reversing the direction in which the gas is taken off a coking charge so as to equalise temperature conditions and retard local over- or under-heating.[98]

Some attention has been given to the possibility of using the sensible heat of coke discharged from ovens by circulating flue gas or inert gas through the charge in a chamber. The gases afterwards pass through feed-water heaters and waste-heat boilers. The whole are mounted on movable cars.[99]

WATER-GAS.

The Research Sub-committee of the Gas Investigation Committee of the Institution of Gas Engineers has carried out a series of tests on a Humphries and Glasgow water-gas plant at Birmingham.[100] The object was to obtain the thermal efficiency of the blue water-gas process for purposes of comparison with the efficiencies obtained in steaming vertical retorts. The mode of carrying out the tests and the results are exhaustively described. The normal cycle used was one consisting of a one-minute blow, and a four-minute run which included a 2½-mins. down run. Up-runs were resorted to before clinkering to cool the lower part of the fuel bed. The average blue gas made contained less than 5% of carbon dioxide, more than 39·5% of carbon monoxide, and over 48% of hydrogen. The blow gases contained about 12% of carbon dioxide, 12·5% of carbon monoxide, 3·0% of hydrogen, and 0·5% of methane. From 57,500 to 60,800 cub. ft. of 293–306 B.Th.U. gas was obtained per ton of coke (dry and ash-free) giving 38·92 to 36·81 lb. of coke per 1000 cub. ft. Interesting figures are tabulated in regard to the distribution of carbon, sulphur, and nitrogen. The sulphur equivalent to the ammonia at the inlet of the scrubber amounted to 0·74 lb. per ton of coke charged to generator. Dust collected

[97] *Gas World*, 1921, *Coking Sect.*, March 5, p. 13.

[98] H. Koppers, U.S.P. 1,369,673; *J.*, 1921, 251A.

[99] Gewerkschaft Emscher-Lippe and H. Heyn, E.P. 153,313; *J.*, 1921, 424A.

[100] *Sixth Report*; *Gas J.*, 1921, **154**, 619, 672; *J.*, 1921, 649A.

at various places after the scrubber largely consisted of silica. Similar deposits have been previously observed. The thermal efficiency, taking the fuel for steam supplied to generator and turbine into account, was 45·8–46·7%, and when this was not allowed for reached 55·2–55·9%. No allowance is made for picking coke from ashes or recovery of potential and sensible heat from the blow gases. The latter important loss could be made use of in waste-heat boilers which it is calculated would give 69–78 lb. of steam per 1000 cub. ft. of water-gas made. The average efficiency would then be 55·9%. This does not compare very favourably with the steaming tests at Uddingstone. E. G. Stewart, however, previously obtained a better waste heat recovery of 90 lb. of steam at 100 lb. pressure per 1000 cub. ft. with a somewhat lower amount of heat in the waste gas and maintains that the efficiency of the water-gas plant should be 70%.[101]

It is reported that at Brentford and Southall waste-heat boilers have resulted in surplus steam over that required for the plant.[102] The introduction of waste-heat boilers coupled with the system of feeding the generator direct with hot coke from horizontal retorts at these works must bring up the efficiency considerably. The process then becomes one of two-stage gasification and leads naturally *via* the Robinson plant to complete gasification. The advantage of the two-stage process will lie in the fact that the yield of by-products will be higher and they will be more easily recovered in this way.

An interesting matter which should receive further attention is the part played by mineral matter in the gasification of solid fuel. Thus L. Vignon[103] finds that the lime at all events plays an important part. It favours the production of methane, and by its catalytic activity carbon monoxide can be decomposed in the presence of steam with production of hydrogen and hydrocarbons. It is considered possible to produce an artificial coal gas in the water-gas plant by bringing the water-gas into contact with lime and steam or by mixing lime with the coke.

Blue water-gas stenches are dealt with in a report from the U. S. Bureau of Mines.[104]

Ethylene.

A further account of the experimental work at Skinningrove on the conversion of ethylene into alcohol is given by C. F. Tidman[105]. Powdered silica was used as a catalyst in the absorption and found

[101] *Gas J.*, 1921, **156**, 203.

[102] *Gas J.*, 1921, **154**, 145.

[103] L. Vignon, *Ann. Chim.*, 1921, **15**, 42 ; *J.*, 1921, 206A.

[104] Allison and Katz, *Tech. Report, No.* 267 ; *Gas World*, 1921, **74**, 440

[105] *J.*, 1921, 86T.

to increase the efficiency 5% with 95·4% sulphuric acid. It is judged that a 3-minutes' contact should give a 70–80% recovery in practice. Diethylene disulphide was isolated as an impurity in the refined alcohol. It is proposed to remove hydrogen sulphide by reaction with sulphur dioxide, the excess of the latter and the free sulphur being removed in scrubbers. The absorption of ethylene and propylene by sulphuric acid has also been investigated by S. G. P. Plant and N. V. Sidgwick.[106] While the absorption increased with stronger acid the amount of diethyl sulphate also increased. The absorption is followed by the reaction of the absorbed ethylene with acid to give ethylsulphuric acid and the latter interacting with ethylene gives rise to diethyl sulphate. Autocatalysis is considered to be well marked with acids of strengths 93·1–99·3% H_2SO_4.

Sulphur Purification.

A process has been suggested for removing hydrogen sulphide by a preferential catalytic oxidation over a layer of activated charcoal, the sulphur being afterwards removed by some suitable solvent.[107] This is somewhat at variance with the work reported by the Alkali Inspector,[108] who finds that wood charcoal does not behave in an analogous manner to oxide of iron but produces an excessive amount of acid products and a limited amount of free sulphur.

N. E. Rambush, who uses a method of liquid purification by circulating ferric hydrate in suspension, finds that a loss of sulphur occurs during the subsequent oxidation.[109] He therefore maintains a closed circuit so that the oxygen content of the air used for revivification becomes reduced to 8% and is kept at this by renewal with fresh air from time to time. Iron compounds may also be used in alkaline solution, tartrates, oxalates, etc. being added to prevent precipitation of the iron, with a disinfectant to prevent bacterial action.[110]

In the wide field of work still presented by oxide purification, the researches reported by the Alkali Inspector for 1920 are welcome.[111] The material examined designated "burnt oxide" does not appear to be the ordinary burnt spent oxide which has been used in making up artificial oxides, but is a residue of some process which is "activated" by mixing with a small proportion

[106] *J.*, 1921, 14T.

[107] W. Schumacher, G.P. 331,287 ; *J.*, 1921, 338A.

[108] *Alkali Inspector's Report*, 1920, p. 38 ; *J.*, 1921, 571A.

[109] E.P. 162,554 ; *J.*, 1921, 426A.

[110] Badische Anilin u. Soda Fabrik, G.P. 299,163, 331,322, 334,524, 334,525, 333,755 ; *J.*, 1921, 338A, 346A, 470A.

[111] *Alkali Inspector's Report*, 1920, p. 25 ; *J.*, 1921, 571A.

of lime and 10% of fine coal, pressing, and burning. The material was, comparatively speaking, very inactive in the presence of hydrogen sulphide but the absorption was materially increased after repeated use and the colour changes indicated that the surface was being gradually attacked. When a mixture of air and hydrogen sulphide was used a more rapid action was obtained which was apparently limited by the accumulation of residual nitrogen. The action appeared to be a purely catalytic one and it was not impaired by excess of air or hydrogen sulphide, but unfortunately fell off after repeated use. A rise of temperature favoured the reaction.

W. A. Dunkley gives the result of an extensive examination of the subject.[112] He prefers to consider that hydrates of iron of definite composition do not exist except possibly the monohydrate, and that the water which affects the behaviour of the oxide is adsorbed on the surface of the material. For each oxide there is a definite content of water which is most suitable and the activity alters with water content above or below this limit. The yellow oxides are considered as a rule more active than the red and may be worked with a wider range of the water content. By heating to 400° C. such oxides are transformed into reddish varieties and the activity is then less and is not restored on moistening with water or only very slowly. When a hydrated or non-hydrated oxide is sulphided and revivified in presence of water it tends to return to the same physical state, colour, and water content. It is important to note that the oxide fouling tests were carried out at the ordinary temperature and the oxide was not allowed to gather heat from the reaction; hence the activity is limited. This especially applies to the fouling of oxides which have been previously subjected to heat.

A very interesting process is foreshadowed for the removal of hydrogen sulphide by washing the gas with a solution of an organic compound.[113] A saturated solution of methylene blue in an aqueous solution containing 20% of pyridine is given as an example, and certain compounds of the azine, triphenylmethane, and indigoid dyestuffs and other substances which may be reduced by hydrogen and oxidised by air can also be used. Benzol may be added if desired to prevent removal of light oil from the gas. The reduced dyestuff is afterwards re-oxidised by blowing air through the solution and the free sulphur recovered.

Carbon Bisulphide and Cyanogen.

In the removal of sulphur compounds by oil washing E. R. Hamilton[114] reports that the chief trouble experienced in dealing

[112] *Gas J.*, 1921, **150**, 382, 436, 491; *J.*, 1921, 615A.

[113] South Metropolitan Gas Co., E. V. Evans, and H. Stanier, E.P 168,504; *J.*, 1921, 728A.

[114] *Gas J.*, 1921, **155**, 729; *J.*, 1921, 760A.

with gas rich in these compounds was in maintaining a suitable temperature. At a temperature of 70°–75° C., 8 gallons of oil per 1000 cub. ft. was necessary to obtain a 50% reduction. It is considered that the temperature should be kept to about 60° C. for efficient working. Considerable advantage was secured by the simultaneous removal of naphthalene. It has been suggested that the vapours from the distillation of such wash-oil should be passed into sulphuric acid for the purpose of removing thiophene, or an oil should be used which could be washed directly with acid for the same purpose.[115]

The use of dilute hypochlorite solutions for washing the gas to remove sulphur compounds has been investigated, and found possible provided intimacy of contact is obtained.[116]

The simultaneous removal of cyanogen and carbon bisulphide is proposed by M. Minot.[117] The gas, cooled and freed from tar but containing ammonia, is washed with a dilute sodium polysulphide solution obtained from spent oxide :—

$$(NH_4)_2S_2 + HCN + NH_3 \rightarrow NH_4SCN + (NH_4)_2S$$
$$(NH_4)_2S + CS_2 = CS_3(NH_4)_2$$

Secondary reactions occur owing to the oxygen present oxidising the polysulphide to thiosulphate and sulphur, and carbon dioxide which forms an equilibrium in decomposing the polysulphide. The wash liquor is distilled and ammonia driven off to the sulphate plant. The thiocarbonate is decomposed to thiocyanate; the solution is evaporated to dryness and the residue may be converted to ferrocyanide.

Another method of removing cyanogen is to pass the gas through chalk which may be sprayed with water or ammoniacal liquor. The chalk is supposed to act as a catalyst, and free sulphur was found in the residue.[118]

AMMONIA.

Important information as to the compounds of ammonia and carbon dioxide which can exist in contact with aqueous solutions of the components between 0° C. and 60° C. is given by E. Terres and H. Weiser.[119] Five different compounds are recognised as solid phases—ammonium bicarbonate, the bicarbamate-carbonate double salt, the normal carbonate, ammonium carbamate, and the

[115] South Metropolitan Gas Co., E. V. Evans, H. Hollings, and H. Stanier, E.P. 168,482 ; *J.*, 1921, 728A.

[116] E. C. Brenner, *Amer. Gas J.*, 1920, **114**, 339, 348 ; *Chem. Abst.*, 1921, **15**. 1800.

[117] *Chim. et Ind.*, 1921, **6**, 135 ; *J.*, 1921, 726A.

[118] J. G. Taplay, *Gas J.*, 1921, **155**, 589 ; *J.*, 1921, 726A.

[119] *Z. Elektrochem.*, 1921, **27**, 177 ; *J.*, 1921, 431A.

carbamate-bicarbonate double salt. Starting with the first-named and water between 0° C. and 33° C., as the concentration of ammonia increases the solid phases change to the other compounds in the order given.

An interesting plant for the distillation of liquor is described[120] in which the liquor is sprayed successively into chambers at suitable temperatures and diminishing pressure so that the vapours are released in stages. The liquor is preheated by passing through tubes enclosed in the jackets surrounding the spraying chambers through which waste gases are circulated. Provision is made for addition of lime to decompose fixed salts.

A novel idea is put forward to remove impurities by compressing gas in cylinders with glycerin to about 300 lb. pressure and then cooling it in condensers to 60° F. The fog of glycerin with dissolved impurities is separated from the gas, and upon releasing the pressure from the former most of the dissolved gases fly off as vapour and the remainder can be expelled by warming.[121]

By distillation of crude liquor, solutions of various strengths can be obtained which can be used for washing gas free from carbon dioxide and hydrogen sulphide, the gas finally passing through an acid saturator to remove ammonia.[122] Or the residual crude liquor obtained by driving off the greater part of the free ammonia can be used for further washing in the scrubbers until its content of fixed salts is sufficiently high to permit of its being worked up completely. By this method fuel consumption on sulphate plants can be reduced.[123]

Work on the oxidation of ammoniacal liquor previous to distillation is reported.[124]

The neutralising of the free acid in sulphate has not yet become common, but fresh processes have been devised. Thus J. B. Hansford[125] places a catch-box or small saturator above the usual saturator, and works the main saturator up to neutral point. When this point is approached the exit gases which will contain ammonia are passed to the catch box, and there held. When the neutral salt has been removed the catch box is emptied into the main saturator and the process repeated. N. Wilton proposes to place the wet acid salt in a pressure filter and after forcing out the mother liquor by dry steam, admit ammonia gas to neutralise.[126]

[120] Holmes and Co., M. Boocock, and W. Wyld, E.P. 167,719; *J.*, 1921, 431A.

[121] W. O. Felt, E.P. 159,905; *Gas J.*, 1921, **154**, 556.

[122] J. H. Fairweather, E.P. 147,583; *J.*, 1921, 378A.

[123] J. H. Fairweather, E.P. 165,833; *J.*, 1921, 582A.

[124] *Alkali Inspector's Report*, 1920, p. 20; *J.*, 1921, 581A.

[125] *Gas World*, 1921, **75**, 243; *J.*, 1921, 733A.

[126] E.P. 154,328; *J.*, 1921, 44A.

TAR AND TAR PRODUCTS.

New processes have been suggested for distilling tar by hot gas, steam, etc. to avoid the increase in free carbon and pitch which occurs in ordinary distillation. In one case an inert gas such as carbon dioxide or nitrogen is used which is constantly drawn off at the outlet of the condensers and recirculated through a heater to a still. It is claimed that the yield of oil is increased, the pitch yield reduced from 60% to 46%, and the free carbon in it from 40% to 28%. Moreover tho distillation can be carried to a much higher temperature and pitches of melting point 350°–600° C. obtained without coking of the residue.[127] In another case preheated tar is injected with superheated steam into a tube so as to be converted to vapour. Carbon is deposited in a dust chamber and the tar oils separated by fractional condensation.[128] Or again, the superheated steam may be passed through the liquid tar at a temperature of 200°–250° C. in a continuous manner. Separation is assisted by fractional condensation which is controlled by adjustment of the outlet temperature of the still. Tars with high water content can be satisfactorily dealt with in this manner.[129] H. Offerman[130] prefers wet steam at 100° C. and finds that higher yields of oil and less pitch result.

An interesting study of the synthesis of anthracene from benzene and ethylene is reported. A mixture of the two vapours was passed through a quartz tube in an electric furnace in the proportion of two of benzene to one of ethylene. The tars collected from experiments made at various temperatures from 800° to 1000° C. were analysed, and the anthracene content found to reach a maximum at 925°. Above this temperature carbon rapidly separated. At 925° C. the tar contained 4·45% or 0·675% on the benzene. At 1000° C. the yield of anthracene was zero.[131]

The crystallising properties of solutions of anthracene, phenanthrene, and carbazole have been studied by E. Pascal,[132] and the melting points and boiling points by W. Kirby.[133]

The product obtained by oxidising anthracene oil after the phenols have been extracted is said to be suitable for transformer oil.[134] By heating with sulphur with or without air, anthracene and phenanthrene are converted into pitchy substances which

[127] Barrett Co., E.P. 158,852; *J.*, 1921, 575A.

[128] W. Anderson and J. Meikle, E.P. 158,337; *J.*, 1921, 209A.

[129] M. de Savignac, *Gas J.*, 1921, **155**, 545.

[130] *Chem.-Zeit.*, 1920, **44**, 773; *J.*, 1921, 35A.

[131] J. E. Zanetti and M. Kandell, *J. Ind. Eng. Chem.*, 1921, **13**, 208; *J.*, 1921, 253A.

[132] *Bull. Soc. Chim.*, 1921, **29**, 644; *J.*, 1921, 686A.

[133] *J.*, 1921, 274T.

[134] M. Melamid, E.P. 143,193; *J.*, 1921, 173A.

increase the lubricating properties of the oil, and render it suitable for lubricating ropes, axles, briquette rolls, etc.[135]

H. Tindale separates pitch into four constituent oils boiling up to 300° C., free carbon, petrolenes, and asphaltenes. The latter is most desirable for road tars. In horizontal-retort tars this constituent amounts to 35–40%, in vertical-retort tars to 25–30%. It is proposed to continue the distillation beyond the usual point using superheated steam and air. The latter increases the amount of asphaltenes and the process is continued until the desired product results.[136]

Corrosion.

An examination of several points in connexion with the external corrosion of service pipes has resulted in some interesting observations.[137] With acid conditions bacteria were found to play an important part. In alkaline soils when moisture was present equally severe corrosion occurred, the agent in this case being calcium bicarbonate.

[135] F. S. Schreiber, G.P. 330,970; *J.*, 1921, 339A.
[136] E.P. 163,199; *J.*, 1921, 463A.
[137] J. G. Taplay, *Gas J.*, 1921, **156**, 210; *J.*, 1921, 760A.

MINERAL OILS.

By J. E. Hackford,

Chemical Adviser to H.M. Petroleum Department.

The Origin of Petroleum.

The most gratifying feature of the year has been the recognition by the various authorities that they must devise a theory as to the mode of formation of the petroleum oil particular to the district in which they are interested, and not, as at the present time, to attempt to build up a single theory as to the formation of petroleum oils in general. There is some significance in the fact that those opinions which attribute the formation of petroleum to vegetation, on account of the optically active constituents which have been identified, all originate from the East. Whilst it is true that this phenomenon has been discussed in the West, American workers have not put forward any serious theory, supported by observation, in this direction. Another point of interest is that most of the work done in connexion with this theory has been undertaken by men who, presumably, have lived in the atmosphere of the Russian and Galician oilfields. It is here suggested that these theories have originated owing to work accomplished on that class of oils loosely known as the naphthenic oils, and that such theories apply to the oils in question. W. Steinkoff, H. Winternitz, W. Roederer, and A. W. Wolynski[1] suggest that the optically active constituents originate from cholesterol and its derivatives, acknowledging, however, the previous work of Engler and Hullard.[2] At the present time, the decomposition products obtained from cholesterol are all dextrorotatory, whereas certain fractions of petroleum have been found to be lævorotatory. By heating cholesterol at a temperature of 150° C. with kieselguhr, cholesterylene is formed, and there is a gradual diminution to a minimum value of the lævorotatory power of the cholesterol. This is not due to racemisation, since an increase ultimately occurs. By heating cholesterol in the presence of quartz, at a temperature of 200° C., the rotation continuously diminished, and was ultimately converted into a dextrorotation. During these heating processes, decomposition of the cholesterol took place, the decomposition products containing

[1] *J. prakt. Chem.*, 1919, **100**, 65.

[2] *Z. angew. Chem.*, 1908, **21**, 1585.

varying amounts of hydrogen, and Steinkoff, Winternitz, Roederer, and Wolyński suggest that, as the result of these changes, the optically active component is generated, since liquid cholesterylene can be reduced in the presence of palladium to a saturated, dextrorotatory, highly viscous product, which exhibits no fluorescence, and which very closely resembles the natural petroleum product separated by Halmai.[3] It is reported that traces of chloresteryl ether were produced when the mixture of cholesterol and kieselguhr was heated at 30° C. for a short time. C. Predescu[4] cites the optical activity of some of the higher boiling fractions of Roumanian petroleums. K. Kobayashi[5] has given a very interesting account of experiments in which he obtained mineral oil, aliphatic and naphthenic acids by the distillation of herring oil in the presence of clay. The hydrocarbons in the oil were mainly of the naphthenic series, together with a considerable quantity of olefines. The formation of the hydrocarbons is attributed to the action of the Japanese acid clay, $Al_2O_3, 6SiO_2, xH_2O$. The fish oil is hydrolysed to fatty acids and glycerol by the action of the water in the clay; and the fatty acids are decomposed into hydrocarbons, by the elimination of carbon dioxide, and with the formation of acetic and naphthenic acids. The hydrocarbons thus formed are cracked to lighter ones by the upper layer of clay. The oil-fields of Japan are associated with the outcrops of Japanese acid clay, and Japanese petroleum is accompanied by salt water. It is suggested that natural processes, similar to those described above, account for the formation of Japanese petroleum from marine animals. In Mexican oils, which there is good reason to believe are derived from marine vegetation, corroborative evidence is given by the presence of iodine in the accompanying salt waters, and a multiplicity of elements, such as could have been derived from marine vegetation, *e.g.* vanadium, gold, molybdenum, lead, and tin in the ash of the oil itself. One of the common omissions from such theories as the above is that of corroborative evidence, and it might be suggested that iodine, which is known sometimes to occur in the livers of certain marine animals, and phosphorus as phosphates, be searched for.

J. E. Hackford[6] explains the formation of various forms of bituminous matter from petroleum, and entertains the possibility of the simultaneous formation of both coal and oil. He puts forward the theory that, in the decomposition of a stratum containing a deposit of either animal remains or vegetable matter, these substances form oil and gas, which, if contained in a sandy bed, are

[3] *Diss., Karlsruhe*, 1909.
[4] *Bull. Sci. Acad. Roumaine*, 1920, **6**, 188; *J.*, 1921, 377A.
[5] *J. Chem. Ind. Japan*, 1921, **24**, 1; *J.*, 1921, 250A.
[6] *Min. and Met.*, No. 163, July, 1920.

swept away from their source, as rapidly as formed, by either gravity or water, since neither the animal remains nor the marine vegetation contain cellulosic material capable of forming a spongelike tissue which would hold the oil *in situ* during the decomposition stage.

Then assume a buried deposit of terrestrial vegetation. Decomposition takes places, resulting in the formation of oil and gas, as in the case of the marine vegetation. Owing to the cellulosic nature of the material the oil is kept *in situ*, whilst decomposition proceeds. Accompanying this decomposition there is probably a rise in temperature, which, even if not above 100° C., is quite sufficient to convert into kerotenes the oxy- or thioasphaltenes that are simultaneously formed with the oil. As the process goes on, the kerotenes become more sparingly soluble, until they are insoluble in pyridine and quinoline, and so remain as a solid in the spongelike mass afforded by the cellulosic structure of the terrestrial vegetation.

P. Carmody[7] also states a view which inclines towards a vegetable origin for all the carbon deposits on or in the earth's crust. The principal chemical constituent of this vegetation is cellulose, which contains 44% of carbon. Coal is also of vegetable origin, and was formed from cellulose, the chemical change probably taking place in the presence of a limited quantity of water. When we come to consider liquid carbon deposits, *e.g.*, petroleum oils, the subject becomes more complicated, as there is no microscopical evidence of cellulosic structure *in situ*, and chemical evidence, in this case, must be mainly relied upon. It is also stated that the presence of an asphaltic base in some oils, and a paraffin base in others, is difficult to understand, unless we assume a difference in the character of the vegetable substances from which the oil was formed.

J. Kewley,[8] whilst referring to the origin of the crude oils of Borneo, states that these oils must be of vegetable origin, as there is no indication in the sands and coals of sufficient animal matter to have yielded such quantities of oil. He states that experience does not lead one to expect that coal and oil were formed simultaneously, although he believes that if the oils in the Kotifield were developed *in situ*, they have either migrated from some distance, or have arisen from the coal, or from the vegetable matter that formed the coal. This latter view was advanced by C. F. Mabery,[9] who stated that coal is, under certain circumstances, an intermediate state of decomposition between vegetable substances

[7] *J. Inst. Pet. Tech.*, 1921, **7**, 308 *et seq.*
[8] *J. Inst. Pet. Tech.*, 1921, **7**, 219.
[9] *J. Amer. Chem. Soc.*, 1917, **37**, 2015.
[10] *J. Inst. Pet. Tech*, 1921, **7**, 407.

and petroleum. W. F. Hume[10] attributes a vegetable origin to Egyptian oil, and points out the proximity of a bituminous coal.

The Oxidation of Paraffins.

A great deal of attention has been centred on the above subject, but the nature of the investigations has been rather to amplify and confirm the work of the previous two years. It will be observed that the interest lies in the countries of central Europe, having originated by the scarcity of fatty acids during and immediately after the war. The aim of the investigators is the production of commercial supplies of fatty acids suitable for soap-making and other industrial uses.

In many of the earlier experiments, the oxidations were carried out by passing air through various petroleum products, at temperatures ranging from 100° to 200° C., with or without a catalyst.[11]

In recent work, the paraffin products were either treated along the same lines, or chlorinated before treatment. A. Schaarschmidt and M. Thiele[12] treat paraffin wax with chlorine, and hydrolyse the resultant chloroparaffins with alcoholic potash. The resultant olefines are oxidised with potassium permanganate, and yield an acid $C_{24}H_{29}COOH$, which was isolated as the silver salt. Oxidation of olefines containing a considerable number of double bonds yields large quantities of acids soluble in water and much carbon dioxide. G. Teichner[13] and Deutsche Erdöl A.-G.[14] have also patented similar processes. A. Grün and T. Wirth[15] show that the oxidation of paraffin wax at 160° C. is practically unaffected by ultra-violet light.

V. Kohlschütter and A. Frumkin[16] show that when petroleum products are subjected to the action of canal rays the cathode becomes coated with substances which, upon heating, evolve gas and tar, leaving a deposit of carbon. From the description given these deposits appear to be asphaltenes, similar in properties to the sludges obtained in transformer oil.

C. Gränacher[17] treated paraffin wax with air containing 2% of nitrogen peroxide and obtained yields of acetic, butyric, and higher fatty acids, with 15% of unsaponifiable oil. The reaction proceeds at 110°–150° C., requiring periods from 10 to 24 days, according to temperature. With pure nitrogen peroxide, oxidation is complete

[11] M. Bergmann, *Z. angew. Chem.*, 1918, **31**, 68. F. Fischer and W. Schneider, *Ber.*, 1920, **53**, 922. A. Grün, E. Ulbrich, and T. Wirth, *Ber.*, 1920, **53**, 987.

[12] *Ber.*, 1920, **53**, 2128; *J.*, 1921, 3A.

[13] E.P. 148,358; *J.*, 1921, 729A.

[14] E.P. 148,892; *J.*, 1921, 729A.

[15] *Z. angew. Chem.*, 1920, **33**, 291; *J.*, 1921, 3A.

[16] *Ber.*, 1921, **54**, 587; *J.*, 1921, 340A.

[17] *Helv. Chim. Acta*, 1920, **3**, 721; *J.*, 1921, 4A.

in 8–10 hours at 140° C., nitric oxide being evolved. Nitrogen, hydrogen cyanide, and nitro-compounds are apparently also formed under these conditions, and the solution of the oxidised wax in caustic soda is red. Pure *n*-undecane treated with nitrogen peroxide at 140° C. gave nonoic acid and lower fatty acids, 40% being unacted upon. This method will, therefore, not give any definite acid from a particular hydrocarbon, and the natural higher paraffins probably only contain small quantities of normal members. A. Schmidt[18] has patented a process for producing fatty acids by passing air through paraffin wax at a temperature of 100°–120° C. in the presence of mercuric oxide as catalyst. W. Schrauth[19] first chlorinates the petroleum fractions, and fuses the monochloro-derivatives at a temperature of 200°–300° C. with alkali, "in such a manner as to avoid high pressure," and obtains a yield of palmitic acids from cetyl chloride. F. Fischer[20] heats paraffin wax in an autoclave with sodium carbonate solution, and blows air through the mixture at a pressure of 30 atmospheres and temperature of 170° C. The fatty acids have an average molecular weight of 250, and are suitable for the manufacture of soap. F. Fischer and W. Schneider[21] discuss the various factors operating during the above process, and find that the molecular weights of the acids were affected by the quantity of air blown through, and a secondary decomposition was produced if the air were blown through in too great a quantity, or for too extended a period. Of the various catalysts used, ceria, fuller's earth, and charcoal gave the best colour, but iron and manganese gave the best yields.

Artificial Lubricating Oils.

Owing to the rapid increase of the use of internal combustion engines, and the limited supplies of crude oils, some apprehension is felt that the day will dawn when the supplies of lubricating oils from natural sources will not meet the demands. This year may claim to have seen the first serious attempt to prepare petroleum products by artificial means, with a view to utilising the products industrially. It is proposed by Tetralin Ges.[22] to treat tetrahydronaphthalene with aluminium chloride at 100° C. and obtain therefrom hydrocarbons, which are claimed to be of use as lubricants. C. Weizmann and D. A. Legg[23] suggest preparing naphthenes by the polymerising action of aluminium chloride on the mixture of butylenes obtained by the dehydration of *n*-butyl alcohol. Under

[18] E.P. 142,507; *J.*, 1921, 74A.
[19] G.P. 327,048; *J.*, 1921, 227A.
[20] *Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 35; *J.*, 1921, 290A.
[21] *Ibid.*, 1919, **4**, 48; *J.*, 1921, 290A.
[22] G.P. 333,158; *J.*, 1921, 341A.
[23] E.P. 165,452; *J.*, 1921, 675A.

the conditions mentioned in the original paper, it is stated that practically quantitative yields of naphthenes were obtained.

K. Oda[24] prepared a quantity of heavy oils by passing purified acetylene over a catalyst prepared by reducing a mixture of nickel and mercury oxides in a current of hydrogen. A. Mailhe[25] obtained a yield of light olefinic and paraffinic oils by passing rape oil over a copper and aluminium catalyst at 550°–650° C.

The above record would be incomplete if no mention were made of the recent methods now employed in the preparation of paraffins by the hydrogenation of coal.[26] The liquefaction of coal by hydrogenating a proportion of its constituents with the formation of liquid tars, oils, and valuable derivatives has attracted considerable attention, but little tangible success has yet been reached. Claims have been made in Germany on behalf of the Bergius process, but no definite scientific information is available. It is stated that coal is treated in suitable autoclaves at 400° C. and at high pressures of hydrogen. (It will be remembered that Berthelot obtained an artificial petroleum by the action of hydriodic acid upon coal in sealed tubes.)

The first of a series of papers by F. Fischer and H. Schrader has recently appeared[27] in which the liquefaction of coal by means of sodium formate is described. Thus, if a Rhenish lignite be distilled destructively about 7% of tar is obtained; but if it be mixed with four times its weight of sodium formate, the yield is 23%–27%, and even greater if the pressure of the gaseous decomposition products and the steam be kept constant. Thus, 45% of tar was obtained from a mixture of one part of lignite and two parts of sodium formate, and 48% from a mixture containing 1 part of the fuel and 8 parts of the salt. The increased production of liquid products is attributed to the influence of the nascent hydrogen formed on the decomposition of the formate used. Molecular hydrogen, as in the Bergius process, is stated to have very little effect.

The experiments can scarcely be said to have progressed far, and it would be useless to criticise the apparent impracticability of the process as it stands at the present moment. It is, however, probable that more economical methods will be discovered which will lead to the same result, namely, the conversion of coal and peat substances into more valuable raw materials. Thus Fischer and Schrader[28] have examined the action of carbon monoxide upon coal during distillation. In the presence of carbon monoxide at

[24] *J. Chem. Ind. Japan*, 1921, **24**, 1161; *J.*, 1921, 836A.
[25] *Comptes rend.*, 1921, **173**, 658; *J.*, 1921, 803A.
[26] *J.*, 1921, 445R.
[27] *Brennstoff-Chem.*, 1921, **2**, 161; *J.*, 1921, 457A.
[28] *Ibid.*, 1921, **2**, 257; *J.*, 1921, 683A.

ordinary pressure little advantage results, but the use of increased pressure and temperatures, such as 500° C., leads to a better yield of tar than when hydrogen is used. The process, however, does not give such successful yields as when sodium formate is employed.

Lubricating Oils.

It is very gratifying to note that there is still considerable interest maintained regarding the causes of the lubricating qualities of lubricating oils.

L. Archbutt[29] expresses the opinion that the measurement of viscosity should be expressed in poises, as was advocated more than 20 years ago by Deeley, and again by Deeley and Parr in 1913. More recently Bingham and Jackson, of the U.S. Bureau of Standards, have proposed as unit the centipoise designated by the letters "cp." to avoid the use of an inconveniently large unit. The generally accepted value of the viscosity of water at 20° C. is 0·01005 poise, and on the centipoise scale this becomes 1·005, and at 20·2° C., 1·000. The viscosity of oils and other liquids, if expressed as centipoises, is therefore accurately stated in terms of the viscosity of water at 20·2° C. taken as unity. The general adoption of the unit would be very desirable, and in the following table the approximate viscosities are given in centipoises of a few well-known lubricating and other oils at different temperatures.

Viscosity in Centipoises.

Water at 20·2° C.=1·000.

Oil.	20°C. (68°F.)	40°C. (104°F.)	60°C. (140°F.)	100°C. (212°F.)
Sperm	36·6	18·5	10·2	4·6
Rape	88·3	39·3	20·7	8·3
Castor	—	239·9	78·7	17·6
Kerosene	1·4	—	—	—
Transformer	27·5	—	—	—
Typewriter	28·9	12·7	6·0	—
Manchester spindle	60·6	23·0	10·9	3·6
Pale machinery (900/7)	90·6	31·5	14·1	4·4
Globe	130·1	40·7	17·3	5·2
Bayonne	167·6	52·2	21·1	6·0
Queen's red (paraff. base)	213·6	63·4	24·6	6·7
Altair (Texas)	397·9	89·1	30·4	7·1
Price's Motorine "C"	—	137·6	50·5	13·2
Mobiloil "BB"	525·7	127·3	46·6	11·6
Valvoline "AA" cylinder	—	235·9	88·3	20·4
"F.F.F." cylinder	—	—	115·5	24·5
"A" cylinder	—	—	125·0	26·9
"S.H.S." cylinder	—	—	184·0	37·1

It would certainly be a great convenience to commerce were the above system adopted, and would obviate the confusion result-

[29] *J.*, 1921, 287T.

ant upon viscosities being expressed in different terms according to the instruments used.

Archbutt recommends the use of the machine designed by Deeley for testing the oiliness of a given lubricant, in distinction to its viscosity. Its design depends upon the fact that when two lubricated surfaces are at rest and in close contact, the static friction or force required to cause movement depends upon the relative slipperiness of the surface. Some very valuable results have been obtained by its use, and the adoption of the machine for commercial purposes is recommended. The views given upon liquid film and solid film deserve special attention.

A. E. Dunstan and F. B. Thole[30] have contributed a valuable paper on the chemical natures of mineral lubricating oils. The keynote of the paper is a discussion of the chemical constituents of lubricating oils. The individual effects upon viscosities are discussed, and it is pointed out that an increase in viscosity occurs concurrently with a decrease in the hydrogen content, and that lubricating oils which still contain a certain proportion of unsaturated hydrocarbons are more viscous than the corresponding saturated oils.

F. H. Garner[31] discusses at some length the causes of carbonisation of lubricating oils in internal combustion engines. He concludes that decomposition of oil in an engine can occur in two ways: (1) Rapid carbonisation due to exposure of particles of the oil in the form of a fine spray or mist to the explosion flame, causing incomplete combustion of the oil. The result of such carbonisation is the production of carbon and asphaltic material; (2) gradual carbonisation of the thin oil film on the piston and cylinder heads at temperatures of 200°–400° C., giving first asphaltic material, which is changed to carbon by the prolonged action of these temperatures.

The writer would here draw attention to the misuse of the word "carbon" as being descriptive of residue produced by the decomposition of lubricating oils in cylinders. A more correct term would be "asphaltum" decomposition products. If an asphaltene soluble in carbon bisulphide be heated for a month, at as low a temperature as 110° C., it undergoes a molecular rearrangement without changing weight. It is then found to be mainly insoluble in this solvent. It cannot be called carbon at this stage, however, for the bulk is still soluble in both chloroform and pyridine, and it is only in extreme cases that the writer has found one of these so-called carbon deposits to contain more than 10% of material insoluble in pyridine. For such substances as are insoluble in carbon bisulphide, but are asphaltic in nature, and which evolve

[30] *J. Inst. Pet. Tech.*, 1921, **7**, 417.

[31] *Ibid.*, 1921, **7**, 98; *J.*, 1921, 138A.

hydrocarbon decomposition products upon dry distillation, the use of the word kerotene is suggested.[32]

Garner reviews the method of determining the asphaltic resin content of lubricating oils, and has adopted a process utilising the selective absorbent power of animal charcoal for these substances. In this respect, however, it is noteworthy that the American Society for Testing Materials have published in their report,[33] their approved tentative method of determining the asphaltene content of a lubricating oil. In this method 10 c.c. of the oil to be tested is measured into each of two clean centrifuge tubes, and diluted to 100 c.c. with a light petroleum naphtha of sp. gr. 0·695–0·705, initial b.p. 45°–55° C., final b.p. 120° C. The tube is then shaken and whirled in a centrifuge at 1400–1500 revs. per minute for 10 minutes. The percentage of asphaltenes is read off in the graduated glass centrifugal bulb.

J. Marcusson[34] confirms these views, naming the mixture of asphaltenes and kerotenes "oilcoals." He states that the deposits generally consist of an oily portion soluble in benzene, a brittle asphaltic constituent insoluble in benzene, a coaly portion, and mineral ash. He also finds that the coaly portion, previously considered insoluble in organic solvents, is soluble in large excess of solvent. From the solution, products of oxidation of mineral oils ("carbenes" or "carboids") and asphaltogenic acids or their anhydrides were separated. The deposit from a hydrogen compressor consisted of 6% of oil soluble in benzene, 8% of black solid material (half saponifiable), soluble in chloroform, and 86% of material insoluble in chloroform. The theory advanced is that by previous long use of the oil, resinification and the formation of asphaltenes, carbenes, and asphaltic acids has taken place.

The report of the Lubricants and Lubrication Inquiry Committee[35] gives some interesting data on the behaviour of various oils at high

	Pressure, tons per sq. in.	Value in c.g.s. units.	Temp., °C.
Castor oil	1·44	227·5	40·2
,,	5·49	864·5	40·0
,,	7·39	1164·0	40·5
,,	Atmospheric	1·94	—
Mobiloil "BB" (mineral)	1·49	227·5	40
,, ,,	4·51	710·0	39·8
,, ,,	6·47	1019·0	40
,, ,,	Atmospheric	1·58	40
Bayonne (mineral)	1	157·5	39·9
,, ,,	4	630·0	40
,, ,,	8	1260·0	40
,, ,,	Atmospheric	0·49	40

[32] *Min. and Met.*, No. 163, July, 1920.

[33] Serial Designation D., 91-21T.

[34] *Brennstoff-Chem.*, 1921, 2, 103; *J.*, 1921, 289A.

[35] Dept. of Sci. and Ind. Research, 1920, p. 80; *J.*, 1921, 36A.

pressure. An apparatus for determining absolute viscosities under high pressures is described, illustrations of the arrangements of the heating walls etc. being given. All the oils tested showed rapid rise in viscosity with pressure.

The densities of oils under pressure were determined by compressing them in a steel cylinder. The densities at 40° C. under pressure are given in the following table :

Pressure. Tons. per sq. in.	Castor oil.	Sperm oil.	Cylinder oil.	Mobiloil (B.B.).
0	0·9415	0·866	0·877	0·899
4	0·9865	0·896	0·904	0·920
8	0·9905	0·9195	0·926	0·949
10	1·001	-	-	-

Tests of the absolute viscosities of rape, sperm, and FFF cylinder oils at high pressure showed that the behaviour of rape and sperm oils is similar to that of castor oil, and that the mineral oil resembled Mobiloil and Bayonne lubricating oil.

The importance of the estimation of the asphaltenes is emphasised by Garner, who found that the formation of carbon in petrol engines accompanied the presence of asphaltenes in lubricating oil. On the other hand, there is no doubt that for conditions such as those of the lubrication of a plain bearing, where heat stresses are not severe, and under conditions in which the oil is not particularly exposed to oxidation, the asphaltic oils give excellent service. The low cold test of good quality asphaltic oils renders them particularly suitable for lubricating purposes where low temperatures may be encountered.

Gasoline Recovery.

A large amount of work has been carried out in the above respect by W. P. Dykema and R. O. Neal,[36] who state that the absorption method of recovering gasoline is more efficient than compression and is applicable to rich gas (2–6 galls. of gasoline per 100 cub. ft.) or to residual lean gases from compression plant. Using naphtha as absorbent, a plant to handle 500,000 cub. ft. can be installed for less than $1000. Details are given of satisfactory units, rates of flow, etc., and the recovery of gasoline from the absorbent by distillation. Portable testing apparatus for determining the gasoline content of natural gas is also described.

F. Bordas[37] describes modifications of current tests to distinguish between blended gasoline and straight-run petrol, owing to the increased fire risk and heavy residue of the former.

G. A. Burrell, G. G. Oberfell, and C. L. Voress[38] describe the absorption of gasoline by the activated charcoal process and its

[36] *U.S. Bureau of Mines, Tech. Paper* 232, 1920 ; *J.*, 1921, 35A.

[37] *Ann. Falsif.*, 1920, **13**, 539 ; *J.*, 1921, 138A.

[38] *Chem. & Met. Eng.*, 1921, **24**, 156 ; *J.*, 1921, 206A.

liberation by means of superheated steam, which expels the absorbed liquid contents. Coconut shell charcoal in granules from 8- to 14-mesh and which has been activated by the steam activation process is best. The charcoal exhibits selective absorption, ethane, propane, and butane being absorbed first and then replaced by heavier fractions. This fact makes it possible to vary the quality of the product by regulating the extent of the absorption. On first coming in contact with the charcoal the gas causes a rise in temperature owing to the liberation of the latent heat of the condensed vapours, but after a few minutes the rise ceases, the heat being used to vaporise lighter fractions previously condensed. A gas rich in gasoline may cause a rise in temperature to 60° C. The efficiency of the absorption is influenced by the temperature of the inflowing gas. At 10° C. there is 100% absorption, but the efficiency falls constantly with rise of temperature. At 300° C. there is no absorption at all. The rate depends on the richness of the gas. A gas giving 400 gallons of gasoline per 1,000,000 cub. ft. may be passed at the rate of 40 cub. ft. per hour per sq. in. of base surface in a 5ft. column of charcoal. After absorption is complete it is necessary to heat to 200° C. to expel the heavy fractions, and the steam employed is heated to 250° C. or higher. The vapour is preferably passed through two condensers in series, the first condensing the major portion of the steam just below 100° C.; in the second cooling water at 15° C. is used to complete condensation. An oil plant and a charcoal on the same gas on the same day gave 125 and 203 gallons of gasoline per 1,000,000 cub. ft. respectively.

The question of the determination of sulphur in light petroleum products has attracted a noticeable amount of attention during the last year. F. Esling [39] describes a modification of the lamp method and advocates particularly care in the selection and the preparation of the wicks. S. Bowman [40] emphasises at some length the disadvantages of the bomb for the estimation of sulphur in petrols and describes a lamp method for this purpose. J. S. Jackson and A. W. Richardson [41] describe a new form of lamp in which the cotton wick is replaced by a bundle of capillaries, sufficient air being injected into the apparatus to enable undiluted spirit to be burnt with a non-luminous flame. This method obviates one of the undesirable points of the lamp method, as the petrol is not fractionated by capillary action or possible selective absorption by the wick. The advantages claimed are: (*a*) The capillaries can easily be taken out and washed and any sulphur held thereon oxidised and included in the estimation. Experiments have shown, however, that the quantities so obtained were negligible;

[39] *J. Inst. Pet. Tech*, 1921, **7**, 83; *J.*, 1921, 500A.
[40] *Ibid.*, 1921, **7**, 334; *J.*, 1921, 878A.
[41] *Ibid.*, 1921, **7**, 26; *J.*, 1921, 207A.

(*b*) the flame is hotter, and therefore the probability of complete combustion is greater. In view of the difficulty of getting glass which will withstand the heat of this flame, it is suggested that the top of the tube be protected by a silica jet; (*c*) much larger quantities of spirit can be burnt in a comparatively short time, thus assuring greater accuracy.

COLOURING MATTERS AND DYES.

By F. W. Atack, M.Sc. Tech., D.Sc. (Manc.), B.Sc. (Lond.), F.I.C.

The year under review has seen disaster approaching in the colour industry of many countries. The industrial slump, leading to a tremendous decline in the consumption of dyes throughout the world, has been coupled with a financial stringency which has necessitated the abandonment by most firms of their research programmes. This has led to a wholesale reduction in the numbers of research and other chemists, up to a point at which it is doubtful whether the colour industry in England is fulfilling its duty, as a so-called "key" industry, to maintain ready for emergencies an adequate supply of well-trained chemists, in return for a Government subsidy.

The attempt of the various concerns not only to supply national demands, but also to provide an export trade,[1] has led to overproduction throughout the world until the supplies available from plants erected would be sufficient at least three-fold for the world's normal annual consumption.[2]

Outside Germany and Switzerland, no really satisfactory progress has been made in the production of vat dyes, and such progress as is to be recorded is mainly along the lines of familiar pre-war German colours. It is clear that immediate commercial and not ultimate national interests are predominant in the control of the chemists' efforts. No fundamental research of importance is in progress with a view to the production of new colours, and it is now clear that the funds provided by the Government for research in the dye industry have been used mainly for so-called "research"—actually obtaining once again the "dye secrets"—leading to the production of well-known colours under various new and novel pseudonyms.

It is unfortunate that this state of affairs was not foreseen, and the public money used in the establishment of a Dyestuffs Research Association under the Department of Scientific and Industrial Research, as free as possible from trade jealousy and interference, to conduct fundamental research along the many lines still open for investigation.

Much has been written of the strong position of the German dye firms, but it is questionable whether the temporary advantage

[1] *See* Chairman's Address, British Dyestuffs Corporation; *J.*, 1921, 133R.
[2] H. E. Fierz, *J.*, 1921, 365R.

they possess of having written off their plant—liable to depreciate so rapidly—could not be met on a more permanent basis by a more careful enquiry into the possibilities of obtaining cheaper raw materials for the industry within the Empire. Freer co-operation between tar distillers and colour makers is obviously essential, but many of the former consider they have not been treated fairly during the war period in regard to estimates of probable requirements, which were generally exaggerated by the colour makers..

A valuable general review of the modern dyestuff industry has recently been given by a recognised Swiss authority,[3] in which the economic situation and future development of the industry are discussed at length. It is stated that the general expenses in the United States are at least five times as great as in Switzerland. The conditions for a successful colour industry are considered to be maintenance of pre-war standards and unceasing progress. Staple dyes may not survive serious competition; thus indigo is meeting strong competition from Hydron Blue, fast blues, and sulphide dyes; alizarin cannot enlarge its field, as strong competitors are appearing; and the tendency to use better and more expensive dyes, which originated in England, will eventually eliminate many of the well-known cheap dyes. In this connexion it may be added that the frank collaboration of a dyer, with a satisfactory knowledge of actual requirements and not only past demand of known colours, and the actual colour chemist in charge is essential for further progress.

The future progress of the dyestuff industry depends largely on tariff questions, a satisfactory tariff making financial interests prepared to advance funds for development work and research.

In England, vital and possibly irreparable damage was done to the dye industry by the failure of the Government to bring into operation at an earlier date the Dyestuffs (Import Regulation) Act, 1920, and, apart from reparation dyes, large stocks of German colours were rushed into the country after the Sankey judgment—stocks which will last for some considerable time even when consumption becomes normal The unfortunate dual position of the Chairman of the Calico Printers' Association as such. and as Acting-Chairman of the British Alizarine Co., Ltd., might have been brought into prominence, and his speech at the general meeting of the Calico Printers' Association[4] has led to several protests, including an important statement by the members of the Dyestuff Group of the Association of British Chemical Manufacturers.[5]

The suggestion that the British Dyestuffs Corporation, Ltd., had been over-capitalised was not considered correct in the Majority

[3] H. E. Fierz, British Association (Section B), 1921; *J.*, 1921, 364R.
[4] *J.*, 1921, 354R.
[5] *J.*, 1921, 366R.

Report of the Sub-Committee on Dyes and Dyestuffs of the Standing Committee on Trusts.[6]

In France, great progress was reported from the extensions carried out at St. Denis during the year 1919.[7]

In the United States it is reported[8] that in the year 1919-20 Switzerland replaced Germany as the chief source of imported colours, and that American makers can now supply certain alizarin colours.

On the occasion of the recent visit of the Society to the United States, it was a matter of frequent comment that the American Chemical Society, as a united body representing both chemical science and industry, was able to bring considerable influence to bear on the Government authorities in matters such as the dye industry,[9] and this is assisted by their admirable publicity system. So far, however, only provisional methods of protection have been granted to the industry. One of the main difficulties experienced by the colour industry is obtaining a supply of anthracene for the production of vat colours, as there is a lack of demand for the hard pitch which remains after the anthracene has been removed from the tar [10]; it is, however, anticipated that the production of anthracene and anthraquinone will soon be sufficient for all requirements,[11] the Thatcher electrochemical process being used for the oxidation.[10]

The German chemical industry has been recovering from the series of crises arising out of the post-war political condition and the exchanges[12]; the temporary difficulties connected with the fuel supply have been largely overcome.[13] The future is regarded with anxiety owing to the difficulty of selling in foreign markets on account of the heavy import duties and the practical prohibition of importation by England and America.[14]

The Swiss dye industry was handicapped at one time by the high value of their currency; a factory has been purchased at Cincinnati, U.S.A., by the controlling interests in Basle.[15]

In Japan, due to a lack of technical skill and of a home supply of intermediates for dye production, it is stated that the industry cannot compete with German or American manufacturers, even with the

[6] *Cmd.* 1370; *J.*, 1921, 255R.

[7] *J.*, 1921, 12R.

[8] *Bd. of Trade J.*, Dec. 9, 1920; *J.*, 1921, 31R.

[9] *Cf. J.*, 1921, 31R, 292R.

[10] *J.*, 1921, 328R.

[11] *J.*, 1921, 292R.

[12] *Chem.-Zeit.*, Jan. 1, 1921; *J.*, 1921, 51R.

[13] "Report on the Industrial and Economic Situation in Germany in December, 1920"; *J.*, 1921, 53R.

[14] *J.*, 1921, 294R.

[15] *Z. angew. Chem.*, Feb. 18, 1921; *J.*, 1921, 130R.

expected 35% import duty[16]; and imports of European and American dyestuffs increased considerably.[17] The suggested amalgamation of dye makers did not materialise, and the view is expressed that some of them only desired it in order to avoid liquidation.[18] It was reported that the Government intend to assist the Japan Dye Manufacturing Co., and considerable progress has been made in the production of the chemicals required in making dyes, but the market is overstocked by the excessive imports, in anticipation of the import duty, during 1920.[19]

In Spain, apart from the simpler colours, recent attempts to establish a colour industry are stated to have been unsuccessful.[20]

In Italy, a crisis in the colour industry has been caused by the total lack of protective duties and the sale of German reparation dyes at cheap rates; the consumption of fast cotton colours and vat dyes, such as indigo and indanthrene, is only small, but it has been announced that these colours are now being made by the Italica and Bonelli companies.[21]

Intermediates of the Aliphatic Series.

Recent developments in the manufacture of synthetic acetic acid[22] are of considerable interest to the colour industry, as apart from its use as such, cheap acetic acid would be of great value as a solvent in many reactions, and also for recrystallisations. The oxidation of acetaldehyde to acetic acid has been effected by treatment with air or oxygen in presence of kieselguhr.[23]

The use of diethyl sulphate in place of the low-boiling ethyl chloride would be preferable for many ethylations for dyestuff intermediates, and further advances towards a cheap technical method of manufacture have been recorded; thus, on passing ethylene in large excess, alone or mixed with an inert gas, into sulphuric acid of about 100% content, or into a solution of ethyl hydrogen sulphate in sulphuric acid, at about 75° C., diethyl sulphate is formed, and may be isolated by extraction, for example, with benzene or ligroin, or the reaction mixture may be used as an ethylating agent without further treatment.[24] A further patent claims the preparation of dialkyl sulphates by the direct action of sulphur trioxide on aliphatic alcohols in presence of dehydrating

[16] *U.S. Com. Rep.*, Nov. 23, 1920; *J.*, 1921, 32R.

[17] *Z. angew. Chem.*, Dec. 24, 1920; *J.*, 1921, 32R

[18] *Chem. Ind.*, March 28, 1921; *J.*, 1921, 157R.

[19] *U.S. Com. Rep.*, April 30, 1921; *J.*, 1921, 235R.

[20] *Z. angew. Chem.*, Nov. 26, 1920; *J.*, 1921, 50R.

[21] *Giorn. Chim. Ind. App.*, April, 1921; *J.*, 1921, 236R.

[22] *J.*, 1921, 345R.

[23] Farbenfabr. vorm. F. Bayer & Co., G.P. 299,782; *J.*, 1921, 717A.

[24] N. V. Sidgwick, S. G. Preston, and A. Boake, Roberts & Co., Ltd., E.P. 157,578; *J.*, 1921, 195A.

agents, such as phosphorus pentoxide or anhydrous sodium sulphate or copper sulphate, and in the presence or absence of inert diluents, such as chloroform, carbon tetrachloride, and the like.[25]

Neutral alkyl sulphates are obtained by distillation *in vacuo* of alkylsulphuric acids in presence of compounds capable of combining with the sulphuric acid formed, *e.g.*, anhydrous sodium sulphate.[26]

A general method for the preparation of amines from aldehydes or ketones is to dissolve the latter in the requisite amount of an 8% solution of ammonia in absolute alcohol, add finely-divided nickel as a catalyst, and then shake the mixture in hydrogen at the ordinary temperature and pressure until absorption of hydrogen ceases, when the amine is isolated in the usual manner.[27]

INTERMEDIATES OF THE BENZENE AND NAPHTHALENE SERIES.

Benzoic acid free from chlorine has been synthesised from benzene by converting sodium benzenesulphonate into benzonitrile (yield 43%) by means of sodium cyanide, followed by hydrolysis with sulphuric acid (sp. gr. 1·6), giving a 95% yield (on benzonitrile) of practically pure benzoic acid.[28]

Aromatic acid chlorides are obtained in good yield by heating the corresponding trichloride (1 mol.) with water (1 mol.) in the presence of sulphuric acid and ferric chloride as catalysts; thus benzotrichloride yields benzoyl chloride, and similarly 2.4-dichlorobenzoyl chloride may be obtained.[29]

Aromatic alkylsulphonamides are obtained by the action of aromatic sulphonic chlorides on alkylamine salts in presence of an acid-neutralising agent such as sodium carbonate; for example, an almost theoretical yield of monomethylxylenesulphonamide is produced from xylenesulphonic chloride and methylamine hydrochloride.[30]

The view expressed by Bucherer that the reactivity of naphthols with bisulphite is due to the intermediate formation of highly reactive naphthyl sulphites is not considered to be in harmony with the established properties of these substances; it is now assumed [31] that the naphthols react in the tautomeric ketonic form, the products being normal additive compounds. Thus hydroxynaphthoic acid and bisulphite react with *as*-methylphenylhydrazine in exactly

[25] L. Lilienfeld, E.P. 143,260; *J.*, 1921, 322A.

[26] E. Kuh, E.P. 149,688; *J.*, 1921, 561A.

[27] G. Mignonac, *Comptes rend.*, 1921, **172**, 223; *J.*, 1921, 194A.

[28] R. H. McKee and F. A. Strauss, *Chem. and Met. Eng.*, 1921, **24**, 638, 697; *J.*, 1921, 410A.

[29] Badische Anilin und Soda-Fabrik, G.P. 331,696; *J.*, 1921, 323A.

[30] British Cellulose and Chemical Mfg. Co., Ltd., W. Bader, and D. A. Nightingale, E.P. 167,941; *J.*, 1921, 749A.

[31] P. Friedländer, *Ber.*, 1921, **54**, 620; *J.*, 1921, 340A.

the same manner as with phenylhydrazine, yielding N-methylnaphthophenocarbazole :—

$$\overline{C_{10}H_6—N(CH_3)—C_6H_4}$$

a reaction which is not possible if Bucherer's views are correct.

Sulphonation.

Contrary to the results of J. N. Ray and M. L. Dey,[32] the sulphonation of benzoic acid in presence or absence of iodine only yields 1% of o-sulphobenzoic acid, and in the sulphonation of catechol the 3-sulphonic acid and not the 4-isomeride is produced.[33] The sulphonation of toluene with chlorosulphonic acid leads to the production of mainly *o*- and *p*-toluenesulphonic acids at low temperatures; at 0° C. and higher temperatures *o*- and *p*-toluenesulphonic chlorides predominate.[34]

Sulphonic acids of monoarylaminoquinones are obtained by the interaction of 2 mols. of a quinone and 1 mol. of an aminoarylsulphonic acid (*e.g.*, sodium sulphanilate) in alcoholic solution; the products serve as dyes, or for the production of mixed diaryldiaminoquinones, either as such or on the fibre.[35]

1-Methyl-2-amino-4-isopropylbenzene-5-sulphonic acid is obtained by heating aminocymene with 98% sulphuric acid.[36]

The exhaustive sulphonation of naphthalene, according to the results of Armstrong and Wynne, could only lead to two products, the 1.3.6-tri- and the 1.3.5.7-tetra-sulphonic acids; the statement[37] that these two acids are accompanied by Senhofer's tetrasulphonic acid[38] could not be confirmed. Losses in the manufacture of H-acid are attributed to the formation of the tetrasulphonic acid and destructive oxidation; in addition small proportions of the 2.7- and 1.6-disulphonic acids are formed, which are only further sulphonated with difficulty to the 1.3.6-trisulphonic acid.[39]

The separation of 1.4.8- and 1.3.8-naphthylaminedisulphonic acids from the crude mixture obtained as described in E. P. 4265 of 1888 has been effected by taking advantage of the differences in the solubility of their barium salts.[40] The product obtained by sulphonating *β*-naphthylamine with 94% sulphuric acid contains

[32] *J.*, 1921, 40A.

[33] V. Auger and M. Vary, *Comptes rend.*, 1921, **173**, 239; *J.*, 1921, 618A.

[34] L. Harding, *Chem. Soc. Trans.*, 1921, **119**, 1261; *J.*, 1921, 715A.

[35] M. Boeke and W. and H. Suida, G.P. 326,511; *J.*, 1921, 174A.

[36] C. E. Andrews, and The Selden Co., U.S.P. 1,314,927; *J.*, 1921, 323A.

[37] G.P. 79,054.

[38] *Monatsh.*, 1882, **3**, 112.

[39] H. E. Fierz and F. Schmid, *Helv. Chim. Acta*, 1921, **4**, 381; *J.*, 1921, 380A.

[40] South Metropolitan Gas Co., and H. Stanier, E.P. 161,859; *J.*, 1921 428A.

35% of the 8- and 65% of the 5-sulphonic acids, together with the 6- and 7-isomerides; the mixed sodium salts are treated with the correct amount of sulphuric acid to precipitate all the 8-sulphonic acid in a practically pure condition; the 5-sulphonic acid is also obtainable pure in this manner, and may be readily isomerised to give the 6- and 7-sulphonic acids.[41]

Methods have been devised for the volumetric estimation of aminonaphtholmono- and di-sulphonic acids by titration with diazo-compounds under suitable conditions.[42]

A method for the detection of naphthalene-2.7- and -1.6-disulphonic acids has been described, based on the preparation of their acetone-insoluble β-naphthylamine salts.[43]

Alkali Fusions.

A method of conducting fusions with molten caustic alkalis has been described in which a hot concentrated solution of a sulphonate, *e.g.*, sodium benzenesulphonate, is introduced slowly on to the surface of the molten alkali.[44]

Diphenyl oxide is prepared by heating an excess of sodium benzenesulphonate with sodium hydroxide, when the sodium phenoxide first produced combines with the excess of sodium benzenesulphonate.[45]

Nitro-compounds.

A continuous process for the nitration of benzene with nitric acid in presence of a mercury compound has been claimed, the cooled liquid being filtered and returned to the nitrator.[46]

The nitration of phenol to picric acid has been investigated, the best results being obtained by sulphonating almost to the disulphonate stage and then nitrating at about 30°–40° C.[47] In the manufacture of picric acid it is proposed to nitrate the sulphonated phenol below 70° C. to the mononitro derivative by means of a slight excess of nitric acid; further nitration is effected above 70° C.[48] Trinitroresorcinol has been obtained by nitrating resorcinoldisulphonic acid, suspended in concentrated sulphuric acid, with 90—100% nitric acid.[49]

The formation of 2.3.6-trinitrotoluene has been considered to occur in the direct nitration of toluene,[50] but the compound formed

[41] G. R. Levi, *Giorn. Chim. Ind. Appl.*, 1921, **3**, 97; *J.*, 1921, 503A.

[42] G. R. Levi, *Giorn. Chim. Ind. Appl.*, 1921, **3**, 297; *J.*, 1921, 686A.

[43] J. A. Ambler, *J. Ind. Eng. Chem.*, 1920, **12**, 1194; *J.*, 1921, 40A. *See also* C. F. van Duin, *Rec. Trav. Chim.*, 1921, **40**, 99; *J.*, 1921, 413A.

[44] B. D. Steele and R. B. Robertson, E.P. 156,269; *J.*, 1921, 142A.

[45] J. M. Johlin and Semet-Solvay Co., U.S.P. 1,372,434; *J.*, 1921, 341A.

[46] T. J. Brewster, U.S.P. 1,380,185; *J.*, 1921, 538A.

[47] F. O. Rice, *J. Amer. Chem. Soc.*, 1920, **42**, 2665; *J.*, 1921, 100A.

[48] T. J. Brewster, U.S.P. 1,380,186; *J.*, 1921, 538A.

[49] W. Friedrich, E.P. 162,578; *J.*, 1921, 463A.

[50] R. B. Drew, *Chem. Soc. Trans.*, 1920, **117**, 1615; *J.*, 1921, 100A.

has in a later publication been considered as more probably the 2.3.4-compound.[51]

2-Chloro-4.6-dinitrotoluene, produced in the nitration of 2-chloro-4-nitrotoluene,[52] has now been obtained to a similar extent in the nitration of 2-chloro-6-nitrotoluene.[53]

o-Nitroanisole is conveniently prepared by adding potassium carbonate and an aqueous suspension of slaked lime to a solution of *o*-nitrochlorobenzene in methyl alcohol, and refluxing with stirring; this method for the continuous generation of caustic alkali is applicable to other condensations involving the elimination of halogen acids in which the presence of an excess of caustic alkali is undesirable.[54]

p-Nitrotoluene-*o*-sulphonic acid is isolated as the sodium salt from the mixture resulting from the nitration at 40°–60° of the product obtained by sulphonating *p*-cymene.[55]

An interesting development which may lead eventually to a new method for the manufacture of β-naphthylamine is disclosed in a method for the manufacture of β-nitronaphthalene, which cannot be obtained by direct nitration; a mixture of mononitrotetrahydronaphthalenes[56] is fractionally distilled and the β-nitrotetrahydronaphthalene separated from the first fraction by freezing is dibrominated; on subsequent distillation *in vacuo*, β-nitronaphthalene is produced.[57]

Nitro derivatives of phenazonium are readily obtained by the action of ferric chloride or concentrated nitric acid on the nitro derivatives of alphyl- or aryl-dihydrophenazines; certain nitro derivatives of alklydihydrophenazines are prepared from mono-alkylated *o*-diamines and picryl chloride or in some cases 2.6-dinitrochlorobenzene, but ring closure has not been effected with 2.4-dinitrochlorobenzene.[58]

The properties of nitroamines and their derivatives have been reviewed. Nitrogen analogues of Stilbene Yellow and Mikado Orange may be prepared from *p*-nitroaniline by similar condensations to those which occur in the stilbene series. Oxidation of *o*-nitroaniline in alcoholic solution with neutral sodium hypochlorite yields 2.2′-dinitroazobenzene, whereas in presence of alkalis a quantitative yield of benziso-oxadiazole oxide is obtained; the

[51] M. Giua, *Gazz. Chim. Ital.*, 1921, **51**, II., 113; *J.*, 1921, 718A.

[52] *J.*, 1920, 623A.

[53] G. T. Morgan and L. A. Jones, *Chem. Soc. Trans.*, 1921, **119**, 187; *J.*, 1921, 210A.

[54] A. V. Blom, E.P. 167,582; *J.*, 1921, 717A.

[55] W. Osakeyhtiö, G.P. 327,051; *J.*, 1921, 173A.

[56] G.P. 299,014; *J.*, 1920, 174A.

[57] Tetralin G.m.b.H., G.P. 332,593; *J.*, 1921, 381A.

[58] F. Kehrmann and J. Effront, *Helv. Chim. Acta*, 1921, **4**, 517; *J.*, 1921, 539A.

dinitro-derivative of the latter yields a brown sulphide dye, thus suggesting an outlet for *o*-nitroaniline.[59]

The colour reactions of a number of nitro-compounds in alcohol or acetone solution with dilute caustic soda have been tabulated, but it is doubtful whether the impurities present in most technical products would not mask these reactions.[60]

The estimation of nitrogen in nitronaphthalenes has been investigated, and a modification of the Dumas method devised to give accurate results; a Kjeldahl method described gives low results, the deficit increasing regularly with nitrogen content in accordance with a graph given.[61] It may be added that nitro-compounds of the anthraquinone series generally give quantitative results by the Kjeldahl method, using additions of potassium sulphate and copper sulphate.

It is a matter of general interest that in a laboratory investigation into the cause of an explosion on a nitration plant, it was found that the presence of lubricating oil in a nitration mixture accelerates the rate of decomposition by acid of the nitro product, *e.g.*, dinitrotoluene.[62]

The importance of a knowledge of the influence of intermediates on chemical workers cannot be over-emphasised; the nature, diagnosis, and prevention of TNT poisoning has been the subject of a very detailed report of which the contents should be noted by all manufacturers of nitro-compounds.[63]

Aromatic Amines.

An almost theoretical yield of aniline has been obtained by passing nitrobenzene vapour mixed with hydrogen over heated fused copper oxide; water-gas or an alcohol, such as secondary butyl alcohol, capable of being dehydrogenated under the conditions of the reaction, may be used in place of hydrogen.[64] A catalytic method for the reduction of, for example, nitrobenzene, consists in adding a small amount of palladium or platinum chloride together with the calculated amount of calcium hydride.[65]

The electrolytic reduction of nitrobenzene to *p*-aminophenol is carried out in 90–91% sulphuric acid using platinum electrodes; a yield of 40–50% is claimed.[66]

[59] F. M. Rowe, *J. Soc. Dyers and Col.*, 1921, **37**, 145; *J.*, 1921, 428A.

[60] O. Rudolph, *Z. anal. Chem.*, 1921, **60**, 639; *J.*, 1921, 729A.

[61] P. H. M.-P. Brinton, F. M. Schertz, W. G. Crockett, and P. P. Merkel, *J. Ind. Eng. Chem.*, 1921, **13**, 636; *J.*, 1921, 652A.

[62] S. Brown, *Chem. Trade J.*, 1920, **67**, 673; *J.*, 1921, 28A.

[63] C. Voegtlin, C. W. Hooper, and J. M. Johnson, *Hygienic Lab., U.S. Public Health Series, Bull.* 126, 1920, 7; *J.*, 1921, 413A.

[64] D. A. Legg and M. A. Adam, E.P. 166,283; *J.*, 1921, 619A.

[65] J. Nivière, *Bull. Soc. Chim.*, 1921, **29**, 217; *J.*, 1921, 409A.

[66] A. S. McDaniel, L. Schneider, and A. Ballard, *Trans. Amer. Electrochem. Soc.*, 1921, 319; *J.*, 1921, 410A.

The reduction of aromatic nitro compounds containing at least one substituent other than the nitro group, and of nitroso or azo compounds, is effected rapidly by means of cast-iron borings and an aqueous solution of a chloride.[67]

Aromatic azo-compounds and nitro-compounds have been reduced to amines by the action of a relatively large amount of iron filings in presence of water and an amount of sulphur dioxide considerably less than would be required to generate sufficient hydrosulphite to effect the reduction; for example, a total yield of *p*-aminophenol amounting to about 80% of the theoretical is obtained by reduction of *p*-nitrophenol, and 2.4-diaminophenol has been produced from dinitrophenol, *o*- and *p*-phenylenediamines from the nitranilines, and anthranilic acid from *o*-nitrobenzoic acid.[68] A similar method for the technical reduction of picric acid to picramic acid[69] has been found preferable to the usual sulphide process; picric acid cannot be reduced directly to triaminophenol with iron and hydrochloric acid, but picramic acid is readily reduced by this process in a similar manner to that used for the production of 2.4-diaminophenol hydrochloride,[70] and the use of triaminophenol for Sulphide Blacks, Nigrosines and azo dyes is suggested.[71]

The reduction of *symm.*-trinitrobenzene to 1-nitro-3.5-phenylenediamine instead of dinitroaniline in aqueous or dilute alcoholic solution by means of ammonium sulphide has been shown to be intimately connected with the formation of addition products of the *symm.*-trinitrobenzene with 2 mols. of ammonia; similarly 2.4.6-trinitrophenol gives 2.6-diamino-4-nitrophenol, and in 2.4-dinitrobenzoic acid the *p*-nitro group, which exerts the strongest action in forming abnormal salts, is reduced.[72] Trinitrotoluene is reduced in acetic acid solution by means of iron and hydrochloric acid to 6-nitro-2.4-diaminotoluene, which is extracted by means of benzene.[73] Reduction by means of iron and hydrochloric acid to triaminotoluene is improved by using only a small quantity of hydrochloric acid, as in the technical reduction of nitrobenzene; triaminotoluene finds application as a dye for cotton, wool, and silk.[74]

Reduction of 2-chloro-4.6-dinitrotoluene with alcoholic stannous chloride gives 6-chloro-2.4-toluylenediamine, which yields azo-

[67] T. S. Moore, E.P. 155,139; *J.*, 1921, 75A.

[68] T. S. Moore, E.P. 165,838; *J.*, 1921, 653A.

[69] G.P. 289,454; *J.*, 1916, 415.

[70] G.P. 269,542; *J.*, 1914, 246.

[71] H. Pomeranz, *Chem.-Zeit.*, 1921, **45**, 866; *J.*, 1921, 686A.

[72] A. Korczynski and S. Piasecki, *Chem. Zentr.*, 1921, **92**, I., 866; *J.*, 1921, 462A.

[73] E. Bielouss, E.P. 137,529; *J.*, 1921, 538A.

[74] E. Bielouss, E.P. 166,934; *J.*, 1921, 688A.

and disazo-derivatives of the Chrysoidine series,[75] similar to those obtained from 2-chloro-4.5-toluylenediamine.[76]

Reduction of nitrobenzene in aqueous emulsion by means of alkali sulphide gives a yield of 72–74% of almost pure crystalline β-phenylhydroxylamine.[77] The method has been extended to *o*-nitrotoluene and to a number of solid aromatic nitro-compounds by dissolving or suspending in 1½–2 times the volume of benzene; *m*-dinitrobenzene and 2.4-dinitrotoluene give mainly the solid dinitro-azoxy compounds, *m*-nitroaniline and *p*-nitroaniline are reduced to the corresponding diamines; the process is not applicable to *p*-nitrophenol.[78]

Full details of process and plant for the production of diphenylamine in 90% yield have been given, using the zinc and ammonium chlorides method.[79]

It is of interest to note that the treatment of 2-chloro-4.5-dinitrotoluene with ammonia or primary amines, such as methylamine or aniline, leads to the replacement of the 5-nitro group, whereas the 6-nitro group is replaced in 2-chloro-5.6-dinitrotoluene.[80]

Methyl derivatives of the xylidines and naphthylamines have been prepared by passing the vapour mixed with methyl alcohol over alumina at 360°–380° C., when a mixture of methyl and dimethyl derivatives is obtained.[81] The catalytic preparation of secondary amines is effected readily in good yield from Schiff's bases of the type $RCH:NR'$ by suspending in the liquid finely-divided nickel and passing in a current of hydrogen. Attempts to alkylate secondary amines further by mixing in vapour form with methyl or ethyl alcohol and passing over alumina at 380°–400° C. failed, the molecule being decomposed; thus benzylaniline and methyl alcohol gave methyl- and dimethylaniline and toluene.[82]

The formation of tertiary amines by the interaction of ethyl or *n*-butyl alcohol with the hydrochlorides of aniline or the toluidines is promoted by the addition of certain catalysts, *e.g.*, cupric chloride, sodium bromide, and calcium chloride, and the use of a large excess

[75] G. T. Morgan and L. A. Jones, *Chem. Soc. Trans.*, 1921, **119**, 187; *J.*, 1921, 210A.

[76] *Chem. Soc. Trans.*, 1902, **81**, 97.

[77] A. Lapworth and L. K. Pearson, *Chem. Soc. Trans.*, 1921, **119**, 765; *J.*, 1921, 538A.

[78] R. D. Haworth and A. Lapworth, *Chem. Soc. Trans.*, 1921, **119**, 768; *J.*, 1921, 538A.

[79] A. Contardi, *Giorn. Chim. Ind. Appl.*, 1920, **1**, 11; *J.*, 1921, 194A.

[80] G. T. Morgan and L. A. Jones, *Chem. Soc. Trans.*, 1921, **119**, 387; *J.*, 1921, 210A.

[81] A. Mailhe and F. de Godon, *Comptes rend.*, 1920, **171**, 1154; *J.*, 1921, 40A.

[82] A. Mailhe, *Comptes rend.*, 1921, **172**, 280; *J.*, 1921, 194A. *See also Bull. Soc. Chim.*, 1921, **29**, 106; *J.*, 1921, 238A.

of the alcohol; *o*-toluidine is the least reactive, the other bases giving 80–90% of the theoretical yield; two new amines have been prepared by this method, viz., di-*n*-butyl-*o*- and -*m*-toluidines.[83]

Arylsulphonyl-1.4-naphthylenediamines and arylenedisulphonyl-*bis*-1.4-naphthylenediamines and their sulphonic acids have been prepared by reduction of the corresponding *p*-azo derivatives or their 2-, 6-, 7-, or 8-sulphonic acids, using reducing agents which are not sufficiently acid or alkaline to effect the hydrolysis of the arylsulphonyl groups; for example, *a*-naphthylamine is condensed with *p*-toluenesulphonic chloride, the product dissolved in sodium hydroxide and treated with benzene-diazonium chloride, when sodium benzene-4-azo-toluene-*p*-sulphonyl-*a*-naphthylamine separates, and is reduced as the free azo compound with zinc and ammonium chloride in aqueous alcoholic solution to toluene-*p*-sulphonyl-1.4-naphthylenediamine.[84] When the sulphonic group occupies position 4 or 5 in the original naphthylamine, 2-azo-compounds are obtained, which on reduction yield derivatives of 1.2-naphthylenediamine; whereas the *para* (1.4) series give yellow diazo derivatives coupling to form azo-compounds with phenols etc., the *ortho* (1.2) series yield non-coupling *ortho*-diazoimides.[85]

Tetrasubstituted ureas are produced by passing carbonyl chloride into a solution of a secondary aromatic amine in a suitable inert solvent, *e.g.*, monomethylaniline gives dimethyldiphenylurea.[86]

Attention may be directed to the treatment of aniline poisoning and preventive measures; the importance of providing satisfactory facilities for rapid treatment appears to be well recognised, and is essential if satisfactory labour is to be available in the industry.[87]

Halogenation.

Toluene, its homologues, and its side-chain substitution products, may be halogenated in presence of an alkali carbonate.[88]

The replacement of sulphonic acid groups by chlorine or bromine occurs generally and may take place with iodine under special conditions; a study of the effect of the presence of other substituents has been made.[89]

[83] A. J. Hill and J. J. Donleavy, *J. Ind. Eng. Chem.*, 1921, **13**, 504; *J.*, 1921, 686A.

[84] G. T. Morgan, and The Imperial Trust for the Encouragement of Scientific and Industrial Research, E.P. 160,583; *J.*, 1921, 381A.

[85] G. T. Morgan and W. R. Grist, *Chem. Soc. Trans.*, 1921, **119**, 602; *J.*, 1921, 464A.

[86] E. I. du Pont de Nemours and Co., A. P. Tanberg, and H. Winkel, E.P. 144,681; *J.*, 1921, 528A.

[87] *J. Ind. Hyg.*, June, 1921; *J.*, 1921, 275R.

[88] C. C. Loomis, and Semet Solvay Co., U.S.P. 1,384,909; *J.*, 1921, 653A.

[89] R. L. Datta and J. C. Bhoumik, *J. Amer. Chem. Soc.*, 1921, **43**, 303; *J.*, 1921, 278A.

Details have been published of the preparation of chloropicrin by the action of chlorine on a cooled aqueous suspension of sodium picrate and similar compounds in presence of sodium carbonate.[90]

Oxidation.

A valuable summary of the recent work on the catalytic oxidation of hydrocarbons, alcohols, and carbon monoxide, using oxides of metals of the fifth and sixth groups of the Periodic Classification, has recently appeared.[91] The importance of temperature control and the form or state of the catalyst is emphasised. Suitable methods for obtaining temperature control in the oxidation of benzene to maleic acid in presence of vanadium oxide have been described.[92] The position with regard to the patents on the air oxidation of naphthalene to phthalic anhydride may be complicated by the publication under the Peace Treaty of a patent with an earlier Convention date, claiming "a suitable catalyst," and specifically vanadic acid at 320°–330° C.[93]

The use of vanadyl chloride has been claimed as a catalyst in the air oxidation of naphthalene, *a*- or *β*-methylnaphthalene, tetrahydronaphthalene, *a*-naphthol, or *o*-xylene to phthalic acid or anhydride.[94]

Oxidation of *o*-cresol in the vapour phase with a gas containing oxygen, in presence of a metallic oxide as catalyst, yields salicyl aldehyde and salicylic acid.[95]

Phthalic anhydride has been obtained by melting *a*-nitronaphthalene with concentrated or fuming sulphuric acid at 150°–160° C., adding a reducing metal, such as iron borings, or zinc dust, and subsequently distilling off under reduced pressure at about 300° C.[96]

Over 80% yield of quinone has been obtained by the electrolytic oxidation of benzene.[97] Electrolytic oxidation of naphthalene in acid solution (mixtures of sulphuric acid and acetone or acetic acid), using a lead peroxide or platinum anode, gives *a*-naphthoquinone together with phthalic anhydride and a dark-brown resinous substance, containing *a*-naphthol and a compound of *a*-naphthol and naphthoquinone; as oxygen-carriers, cerium nitrate,

[90] K. J. P. Orton and P. V. McKie, *Chem. Soc. Trans.*, 1921, **119**, 29.

[91] *J.*, 1921, 307R.

[92] The Barrett Co., E.P. 167,219; *J.*, 1921, 717A.

[93] A. Wohl, E.P. 145,071; *J.*, 1921, 341A.

[94] British Dyestuffs Corp., Ltd., A. G. Green, and J. W. Porter, E.P. 164,785; *J.*, 1921, 561A.

[95] J. M. Weiss, C. R. Downs, and The Barrett Co., U.S.P. 1,380,277; *J.*, 1921, 561A.

[96] H. Sasa, E.P. 140,051; *J.*, 1921, 463A.

[97] H. Inoue and M. Shikata, *J. Chem. Ind. Japan*, 1921, **24**, 567; *J.*, 1921, 652A.

vanadic acid, potassium chlorate and chromate, manganous sulphate, potassium ferrocyanide, and chrome alum were effective in the order given.[98]

The oxidation of carbazole by means of permanganate in boiling acetone solution yields two crystalline isomeric dicarbazyls, $C_{24}H_{16}N_2$, and an amorphous substance; the three substances differ from carbazole in that they do not form picrates.[99]

Hydrogenated Naphthalene Derivatives.

The methods of formation of Δ^1-dihydronaphthalene have been investigated. Isomerisation of the Δ^2- to the Δ^1-isomeride under the influence of alcoholic sodium ethoxide occurs with greater readiness than was previously supposed. Whereas the former yields an additive compound with mercuric acetate, the latter is oxidised by this reagent, which does not react with naphthalene or its tetrahydro-derivative.[100]

Technical naphthalene is purified before hydrogenation by agitation above 100° C. with a finely powdered or porous material, such as fuller's earth, kieselguhr, or animal charcoal, together with either a finely-divided or low-melting metal, *e.g.*, nickel or sodium, or with a metallic amide or carbide, *e.g.*, sodamide or calcium carbide; the product is then distilled under reduced pressure.[101] On heating purified naphthalene under a pressure of 10 atm. to 150°–200° C. with sufficient hydrogen, the desired hydrogenated product is produced, no decahydronaphthalene being formed until all the naphthalene has been reduced to tetrahydronaphthalene.[102] Similar methods have been used for the preparation of hexahydrobenzene from benzene containing thiophen and for the hydrogenation of crude methylnaphthalene.[103]

Tetrahydronaphthalene is prepared by passing a mixture of naphthalene vapour and hydrogen at the ordinary pressure over a mixture of nickel and copper oxides, manganese oxide alone or in admixture with nickel and copper oxides, or an oxide of the rare earths, *e.g.*, thoria or ceria, alone or mixed with one or more of the previously mentioned oxides.[104]

The mixture of 1- and 2-tetrahydronaphthalenesulphonyl chlorides, obtained by the action of chlorosulphonic acid on tetrahydro-

[98] K. Ono, *J. Chem. Soc. Japan*, 1921, **42**, 38; *J.*, 1921, 253A.

[99] W. H. Perkin, jun., and S. H. Tucker, *Chem. Soc. Trans.*, 1921, **119**, 216; *J.*, 1921, 209A.

[100] F. Straus and L. Lemmel, *Ber.*, 1921, **54**, 25; *J.*, 1921, 142A. *See also* F. M. Rowe, *J.*, 1921, 58T.

[101] Tetralin G.m.b.H., G.P. 324,862-3; *J.*, 1921, 253A.

[102] Tetralin G.m.b.H., G.P. 324,861; *J.*, 1921, 253A.

[103] Tetralin G.m.b.H., G.P. 305,104; *J.*, 1921, 687A.

[104] A.-G. für Anilinfabr., G.P. 298,541, 298,553, and 301,275; *J.*, 1921, 294A.

naphthalene at a low temperature, is hydrolysed by steam, and the 1-isomeride separated by its lower solubility in chloroform; the sulphonamides, anilides, and sulphinic acids have also been prepared.[105]

Derivatives of tetrahydronaphthalene have been nitrated as previously described[106] to prevent oxidation and resinification.[107] The reduction products of the nitrotetrahydronaphthalenes are not only the corresponding amines, but intermediate products have also been obtained, such as hydroxylamines, which undergo the usual intramolecular conversion, azoxy-, azo-, and hydrazo-compounds, of which the last-named undergo the benzidine transformation.[108]

On treating *ac*-$\alpha\beta$-dibromotetrahydronaphthalene[109] with water, alcohols, or acids, with or without addition of inactive solvents, the α-bromine atom is replaced by —OR or —O.CO.R (R=hydrogen or alkyl group), whilst the β-bromine atom remains in the molecule.[110]

ar-α-Tetrahydronaphthalenecarboxylic acid is prepared by the action of dry carbon dioxide on dry sodium *ar*-α-tetrahydronaphtholate; on coupling with diazotised nitranilines or their derivatives, it yields azo dyes fast to light and milling.[111]

INTERMEDIATES OF THE ANTHRACENE SERIES.

The purification of anthraquinone is effected by agitating a hot solution of crude anthraquinone in a neutral solvent, such as chlorobenzene or solvent naphtha, with a purifying agent, such as an alkali or alkaline-earth oxide or carbonate or sulphuric acid; the anthraquinone solution is separated, and the solvent removed by steam distillation.[112]

By condensing anthranol or its substitution products with formaldehyde in alkaline or acid solution, with the exception of concentrated sulphuric acid, but including specifically a mixture of glacial acetic acid and concentrated hydrochloric acid, methyleneanthraquinone and its substitution products are obtained, which serve as intermediates in the manufacture of vat dyes.[113]

The dinitroanthraquinones obtained by direct nitration of anthraquinone have been investigated by reduction and conversion of the mixed diamino-derivatives into dihydroxy-compounds,

105 Tetralin G.m.b.H., G.P. 336,615; *J.*, 1921, 575A.
106 G.P. 299,014; *J.*, 1920, 174A.
107 Tetralin G.m.b.H., G.P. 326,486; *J.*, 1920, 174A.
108 Tetralin G.m.b.H., G.P. 337,157; *J.*, 1921, 341A.
109 G.P. 316,218; *J.*, 1920, 360A.
110 Tetralin G.m.b.H., G.P. 335,477; *J.*, 1921, 503A.
111 Farbenfabr. vorm. F. Bayer und Co., G.P. 335,602; *J.*, 1921, 503A.
112 Kinzlberger u. Co., E.P. 143,885; *J.*, 1921, 5A.
113 K. H. Meyer, G.P. 330,550; *J.*, 1921, 254A.

which were separated into the 2.6-, 1.8-, 1.6-, 1.7-, and 2.7-isomerides. From the results it was calculated that 37% of both 1.5- and 1.8-dinitroanthraquinone is obtained together with smaller amounts of the other isomerides. The presence of the 1.2- and 1.3-dinitro-compounds mentioned by Dhar[114] is controverted.[115]

An attempt has been made to determine the *rôle* played by mercury in the α-sulphonation of anthraquinone, the products in absence of mercury being β-sulphonic acids; it is stated that in either case the first product is the α-acid, but that at the higher temperature required in the absence of mercury the velocity of transformation of the α-acid into the β-acid is as great as the velocity of sulphonation; in the presence of mercury but at the higher temperature, the product is also the β-acid, and a higher yield is claimed.[116] (*Note.*—In abstracting this paper for the American Chemical Abstracts, the abstractor correctly adds a warning that the solubilities of the sodium salts of the α- and β-acids have been confused, and the above statements should be accepted with much reserve in view of the complicated reactions which occur on sulphonation of anthraquinone.)

Nitration of 1-hydroxyanthraquinone with nitric acid (sp. gr. 1·52) in sulphuric acid solution yields the 2.4-dinitro-compound.[117] Nitro-derivatives of β-azides of the anthraquinone series are obtained by direct nitration, the nitro-group entering the α-position adjacent to the β-azido group; on reduction by means of sodium sulphide, 1-nitro-2-azidoanthraquinone, for example, gives 1.2-diaminoanthraquinone.[118]

1.3-Diaminoanthraquinone has been prepared by heating with 96% sulphuric acid 1.3-anthraquinone-ditolylsulphamide, obtained by heating 1.3-dibromoanthraquinone with p-tolylsulphamide in nitrobenzene solution in presence of potassium carbonate and copper powder. The 1.6- and 1.7-isomerides were prepared by heating the corresponding nitrosulphonic acids[119] with ammonia under pressure.[120]

The elimination of halogen on the reduction of p-halogenated nitroanthraquinones has been noted; thus 1.4-nitrobromoanthraquinone gives on reduction α-aminoanthraquinone.[121]

[114] *Chem. Soc. Trans.*, 1920, **117**, 1001; *J.*, 1920, 685A.

[115] M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 628; *J.*, 1921, 340A.

[116] A. Roux and J. Martinet, *Comptes rend.*, 1921, **172**, 385; *J.*, 1921, 209A.

[117] F. Ullmann, G.P. 332,853; *J.*, 1921, 381A.

[118] Farbenfabr. vorm. F. Bayer u. Co., G.P. 337,734; *J.*, 1921, 620A.

[119] Clauss, *Ber.*, 1882, **15**, 1514.

[120] M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 71; *J.*, 1921, 462A.

[121] M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632; *J.*, 1921, 340A.

The dibromoanthraquinone used by Graebe and Liebermann in their classical synthesis of alizarin has been shown not to be the 1.2-derivative, as has been assumed; the two products they are stated to have used are not identical, direct bromination of anthraquinone at 100° giving the 2.7-isomeride, whereas oxidation of tetrabromoanthracene gives mainly the 2.3-isomeride.

A patent of a distinctly novel character discloses an interesting isomerisation in the anthraquinone series. It was already known[122] that α-bromo-aminoanthraquinones may be converted by heating in presence of a suitable medium into β-bromo derivatives in cases where a β-position is vacant in the *ortho*-position with respect to the amino group. It has now been found that, on heating α-halogen derivatives of anthraquinone with concentrated sulphuric acid at about 200° C., β-halogen derivatives are produced; for example, 1-chloroanthraquinone gives 2-chloroanthraquinone, and 1.5-dichloroanthraquinone gives 2.6-dichloroanthraquinone. A further example states that 1.6-dichloroanthraquinone gives 3.6-dichloroanthraquinone (usually known as 2.7-dichloroanthraquinone). It follows that a *meta*- and not an *ortho*-isomerisation is under consideration.[123] The yields are not quantitative, and a certain amount of free chlorine is always noticeable during the isomerisation. The latter might indicate an actual migration of the chlorine atom, although in that case an almost quantitative yield would be anticipated. An alternative explanation could be based on the splitting of one of the CO-groups adjacent to the α-halogen, to give an intermediate halogenated benzoylbenzoic acid, followed by condensation to give the β-halogen derivative, in the same manner that *o*-chlorobenzylbenzoic acid gives β-chloroanthraquinone. Such an explanation scarcely seems feasible to explain the direct conversion of $\alpha\alpha$-dihalogen-compounds into $\beta\beta$-dihalogen-anthraquinones.

The replacement of a hydroxyl group in anthraquinone derivatives by chlorine has been effected by treatment with arylsulphochlorides in presence of acid-combining substances; for example, using potash, 1-chloro-2.4-dinitroanthraquinone is obtained from 2.4-dinitro-1-hydroxyanthraquinone, whereas, using diethylaniline, a good yield of 1.2-dichloro-4-nitroanthraquinone is obtained.[124]

Benzanthrone is purified by dissolving in hot halogenated derivatives of aromatic hydrocarbons, separating the insoluble impurities, and allowing the solution to cool.[125]

Semiazoanthraquinones or their derivatives are formed by the action of bromine on α-aminoanthraquinone or its derivatives

[122] G.P. 275,299; *J.*, 1914, 783.

[123] F. W. Atack and G. W. Clough, E.P. 169,732; *J.*, 1921, 840A.

[124] F. Ullmann, G.P. 332,853; *J.*, 1921, 381A.

[125] L. C. Daniels, and National Aniline and Chemical Co., U.S.P. 1,365,024; *J.*, 1921, 142A.

in presence of alkali; for example, the action of hypobromite on finely-divided 1.5-diaminoanthraquinone gives 1.5-disemiazoanthraquinone. On dissolving in sulphuric acid, the corresponding amino-hydroxy-compounds are obtained; thus 1.5-disemiazoanthraquinone gives 1.5-diamino-4.8-dihydroxyanthraquinone, but in case the *p*-position is occupied, the hydroxyl group enters the *o*-position with respect to the amino-group.[126]

Anthraquinonylbenzohydroazines of the formula,

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2\left\langle\begin{matrix}NR\\NH\end{matrix}\right\rangle C_6H_4$$

similar to the products described in G.P. 329,246[127] are produced by heating 1-halogen-anthraquinones or derivatives containing a reactive substituent in *o*-position to the halogen atom, with *o*-aminodiarylamines or their nuclear substitution products, alone or in an inert solvent or suspension medium, and with or without addition of catalysts and substances capable of combining with acids. 1-Chloro-, 1.2-dichloro-, and 1-bromo-2-methoxyanthraquinone give with *o*-aminodiphenylamine the same product, $C_{26}H_{16}O_2N_2$, whereas 1.5- or 1.8-dichloroanthraquinone gives isomeric monochloro-derivatives of this substance; both chlorine atoms are replaced in the case of 1.4-dichloroanthraquinone.[128] Identical products are obtained by condensing primary aromatic amines by means of caustic potash with arylaminoanthraquinones, or their nuclear substitution products, containing a reactive substituent in the *ortho*-position to the imino-group.[129]

Condensations.

A process for the manufacture of phthaleins is claimed using an anhydrous aromatic sulphonic acid, with or without zinc chloride, as condensing agent; the product from phthalic anhydride, phenol, and toluenesulphonic acid, with or without anhydrous zinc chloride, is stated to be particularly free from tarry by-products and from *ortho*-condensation products.[130] An improved yield of phenolphthalein—up to 40% of the theoretical—is obtained by using anhydrous aluminium chloride as catalyst, phenol being present in slight excess; ferric chloride was not so satisfactory. The method described by M. Copisarow[131] is considered to be more efficient and economical.[132]

[126] Farbenfabr. vorm. F. Bayer u. Co., G.P. 335,010; *J.*, 1921, 465A.
[127] E.P. 3347 and 100,581 of 1915; *J.*, 1916, 831.
[128] Badische Anilin- u. Soda-Fabrik, G.P. 329,247; *J.*, 1921, 429A.
[129] Badische Anilin- u. Soda-Fabrik, G.P. 332,013; *J.*, 1921, 429A.
[130] Monsanto Chemical Works, E.P. 157,030; *J.*, 1921, 174A.
[131] *J.*, 1920, 360A.
[132] C. F. Ward, *Chem. Soc. Trans.*, 1921, **119**, 850; *J.*, 1921, 538A.

Condensation of aromatic aldehydes or ketones, containing an amino group in the *o*-position, with methazonic acid, $NOH : CH.CH : NOOH$, yields 3-nitroquinoline or its derivatives; thus *o*-aminobenzaldehyde gives 3-nitroquinoline, isatin gives a mixture of 3-nitro-4-quinolinecarboxylic acid and β-isatinoxime.[133]

Aromatic triazoles (pseudoazimides) are obtained by treatment of *o*-aminoazo dyestuffs, particularly those containing additional amino or hydroxyl groups, with ammoniacal solutions of copper and are to be used as intermediates.[134]

The synthesis of alkylarylmethanes by the condensation of ketones with phenols has been investigated, and yields over 90% obtained by using hydrochloric acid containing a small amount of ferric chloride as catalyst.[135]

Colouring Matters.

The determination of the constitution of dyes from their absorption spectra has been further investigated by F. Kehrmann and his co-workers.[137] It is considered possible to express the constitution of the majority of dye salts only by means of the quinoid formula, and that this formulation is the most satisfactory until Werner's and the quinonoid theory have been brought into better harmony.[138]

Groups similar in behaviour to auxochromes which exhibit increased auxochromic character due to containing true auxochromes, have been termed combined auxochromes; the dimethoxystyryl group has been examined, using the *p*-nitrophenyl residue as chromogen, and is regarded as a new auxochromic unit; combined auxochromes are also able to facilitate fluorescence.[139]

Azo Dyes.

The use of aromatic acylamines as azo components has been investigated, and the auxochromic power of the groups was found to diminish in the order:

$$-OH,\ -NH.SO_2.C_6H_4.CH_3,\ -NH.CO.C_6H_5,\ -NH.CO.CH_3;$$

diazotised *p*-nitraniline couples with *p*-toluenesulphon-α- and -β-naphthylamides to give compounds of the type

$$O : N.C_6H_4.N : N.C_{10}H_6.N : S(:O).C_6H_4.CH_3$$

$$O\ .\ .\ .\ Na\ .\ .\ .\ O$$

[133] Badische Anilin- u. Soda-Fabrik, G.P. 335,197; *J.*, 1921, 463A.

[134] Kalle u. Co., G.P. 338,926; *J.*, 1921, 749A.

[135] A. Muller, *Chem.-Zeit.*, 1921, **45**, 632; *J.*, 1921, 575A.

[137] F. Kehrmann and H. Goldstein, *Helv. Chim. Acta*, 1921, **4**, 26; *J.*, 1921, 174A. F. Kehrmann and M. Sandoz, *ibid.*, 31; *J.*, 1921, 174A.

[138] F. Kehrmann, *ibid.*, 1921, **4**, 527; *J.*, 1921, 539A.

[139] H. Kauffmann, *Ber.*, 1921, **54**, 795; *J.*, 1921, 341A.

[140] W. König and K. Köhler, *Ber.*, 1921, **54**, 981; *J.*, 1921, 428A.

and as the reaction does not occur with the corresponding methylnaphthylamides, it is considered that the naphthylsulphonamide couples in its enolic form, $C_{10}H_7.N : S (: O) (OH)\cdot C_6H_4\cdot CH_3$. Carboxyamides only couple very slowly with diazotised *p*-nitraniline.[140]

A number of azo dyes derived from diazotised 6-nitro-*m*-4-xylidine have been described; resorcinol yields a dye giving full orange shades on chromed wool, and deep yellow shades are produced in case salicylic acid is used.[141]

Azo dyes are obtained by coupling diazotised aminocymene either with an aromatic hydroxy-compound in alkaline solution, or with an aromatic amine of the benzene or naphthalene series or with an aminosulphonic acid in acid solution; β-naphthol gives a bright orange-red dye, and cymene-azo-toluylenediamine is a yellow-brown dye.[142] Similarly dyes are produced from tetrazotised dimethyldi-isopropylbenzidine,[143] obtained by the benzidine transformation from hydrazocymene, produced by alkaline reduction of crude mononitrocymene.[144]

Blue shades fast to light and milling on wool from an acid bath are given by the azo dyes produced by coupling a diazo-compound of 1-amino-4-nitrobenzene-2-sulphonamide, in which one or both hydrogen atoms of the amino-group are substituted by alkyl, aryl, or alkaryl groups, in acid solution with a 2-naphthylamine sulphonic acid or a derivative thereof, or a 2-amino-8-naphthol-sulphonic acid; the nitro-group in these dyes may be reduced by hydrosulphite, when the products dye wool from an acid bath level bluish shades fast to milling and light.[145]

Azo dyes, giving orange to bordeaux shades on wool, and yellow to bordeaux shades on chromed wool, are obtained by coupling a diazo-aryl-sulphonic or -carboxylic acid, which may or may not contain a hydroxyl group, or a substitution derivative thereof, with 8-hydroxyquinoline or its 5-sulphonic acid.[146]

5-Aminodihydroquinine and the corresponding derivatives of other cinchona alkaloids couple with diazotised amines to give azo dyes containing a remarkably labile amino group, apparently in part a function of the quinoline nucleus, as 5-aminoquinoline behaves in a similar manner; the presence of a methoxy or ethoxy group in position 6 facilitates the replacement of the amino group.[147]

[141] S. A. Pearman, *Chem. Soc. Trans.*, 1921, **119**, 717; *J.*, 1921, 464A.

[142] C. E. Andrews and The Selden Co. U.S.P. 1,314,921-2; *J.*, 1921, 294A.

[143] C. E. Andrews and The Selden Co., U.S.P. 1,314,925-6; *J.*, 1921, 294A.

[144] C. E. Andrews and The Selden Co., U.S.P. 1,314,924; *J.*, 1921, 323A.

[145] Farbenfabr. vorm. F. Bayer u. Co., E.P. 164,218; *J.*, 1921, 504A.

[146] Akt.-Ges. f. Anilin-Fabr., E.P. 166,033; *J.*, 1921, 619A.

[147] W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1920, **42**, 2278; *J.*, 1921, 96A.

A monoazo dye, giving bluish-red shades on wool and silk, is obtained by coupling diazotised β-naphthylamine-1-sulphonic acid in alkaline solution with H-acid.[148]

Azo dyes, giving orange-red to blackish-violet shades fast to light and to washing on wool from an acid bath, are produced on coupling diazotised monoacidyldiaminodiarylsulphones, especially the 2.5- and 2.4-compounds, with 2-aminonaphthalene derivatives, especially 2-aminonaphthalenesulphonic acids and 2-aminonaphtholsulphonic acids.[149]

o-Aminoazo dyes are obtained by coupling with diazotised amines or tetrazotised diamines the products formed by coupling 1.8-aminonaphthol-4.6-disulphonic acid in acid solution with diazotised *o*- or *p*-aminosalicylic acid, sulphoaminosalicylic acids, nitroaminosalicylic acids, or amino-*o*- or amino-*m*-cresotic acids.[150]

o-Hydroxyazo dyes are produced by coupling a diazotised *o*-aminophenol derivative containing one or more halogen atoms or nitro groups, or both, or a homologous compound, with an alkaline solution of 8-halogeno-α-naphthol-5-sulphonic acid, giving mordant dyes for wool, of which the chromium lakes possess good fastness; for example, 4-chloro-2-aminophenol yields a dye giving dark-blue shades on chrome-mordanted wool, whereas the corresponding 4-nitro-compound gives a dye producing bordeaux shades on wool from an acid bath which become black on chroming.[151]

The *o*-hydroxyazo dyes, obtained by coupling *o*-hydroxydiazoarylsulphonic acids with 5.8-dichloro-1-hydroxynaphthalene, dye wool from an acid bath, and when afterchromed or dyed and chromed in a single bath, produce reddish-blue, blue, or black shades fast to light and milling.[152] Similar dyes, particularly adapted for dyeing wool in presence of mordants in the same bath, are produced by coupling an *o*-hydroxydiazo-compound which is not sulphonated, such as diazotised 4-nitro-2-aminophenol, with 1-*o*-carboxybenzoylamino-7-naphthol; intense dyes result which dye wool in presence of chromium mordants dark greenish shades of excellent fastness to milling.[153]

Hydroxyazo dyes, giving brown shades on animal fibres in conjunction with metallic mordants, are produced by coupling diazotised *o*-aminophenols, *o*-aminonaphthols, or their nitro, sulphonic, or carboxyl derivatives with 4.6-diamino-1.3-xylene.[154]

[148] A. J. Field, U.S.P. 1,383,711; *J.*, 1921, 620A.

[149] G. de Montmollin, and Soc. of Chem. Ind. in Basle, U.S.P. 1,359,069; *J.*, 1921, 464A.

[150] C. Rudolph, G.P. 298,852; *J.*, 1921, 464A.

[151] Akt.-Ges. f. Anilin-Fabr., E.P. 168,681; *J.*, 1921, 731A.

[152] Akt.-Ges. f. Anilin-Fabr., E.P. 145,053; J., 1921, 619A.

[153] Akt.-Ges. f. Anilin-Fabr., E.P. 145,057; *J.*, 1921, 619A.

[154] G. T. Morgan and British Dyestuffs Corp., Ltd., E.P. 160,848; *J.*, 1921, 341A.

1.8-Dihydroxynaphthalene has been prepared by heating 1.8-dihydroxynaphthalene-4-sulphonic acid with sulphuric acid and water at 150° C.; on coupling with an equimolecular quantity of benzenediazonium chloride preferably in hydrochloric acid solution, 4-benzeneazo-1.8-dihydroxynaphthalene is produced, whereas excess of diazo-compound in acetic acid solution gives 4.5-dibenzeneazo-1.8-dihydroxynaphthalenes. 4-*p*-Sulphobenzeneazo-1.8-dihydroxynaphthalene dyes unmordanted wool a dark cherry red, giving paler shades on aluminium-mordanted wool and dark-brown shades on chrome-mordant.[155]

Diazo-azo-hydroxy compounds are obtained by combining a diazohydroxynaphthalene, for example 1-diazo-5 (or 7)-hydroxynaphthalene or 2-diazo-8-hydroxy-6 (or 3.6-di)-sulphonic acid with a highly reactive monodiazo compound such as *p*-nitrodiazobenzene; the products couple, *e.g.*, with *m*-toluylenediamine, 1-aminonaphthalene-6 (7)-sulphonic acid, or 1-amino-8-hydroxynaphthalene-4-sulphonic acid, to yield dark blue to black substantive cotton dyes.[156]

Readily soluble azo dyes are produced by the action of formaldehyde-bisulphite on diazotisable azo dyes containing at least one external amino-group; alternatively aromatic diazo compounds are coupled with azo components containing an external N-methyl-ω-sulpho group, *e.g.*, from a tetrazotised diamine, such as 3.3′-diamino-4.4′-dimethyldiphenylmethane, and the N-methyl-ω-sulpho derivative of 2-amino-5-hydroxynaphthalene-7-sulphonic acid. The products give yellow to claret shades on cotton, which become extraordinarily fast to washing when diazotised on the fibre and developed with a non-sulphonated azo component.[157]

Disazo dyes which are direct acid dyes for cotton or wool, giving pink to red shades, or may be after-chromed on wool, giving red shades fast to milling, are obtained by combining *p*-disazobenzene-azo-salicylic acid with a 2-naphthylaminesulphonic acid, such as 2-naphthylamine-5- or -6-mono- or -3.6-disulphonic acid.[158]

Disazo dyes, giving on cotton, wool, silk, and other fibres blue shades which can be developed to blue-black to green shades, are produced by diazotising and coupling with 2.8.6-aminonaphtholsulphonic acid the product formed by coupling 1-diazo-4-nitronaphthalene-6 (or 7)-monosulphonic acid with *m*-amino-*p*-cresol methyl ether followed by reduction of the nitro-group.[159]

[155] G. Heller and H. Kretzschmann, *Ber.*, 1921, **54**, 1098; *J.*, 1921, 428A.

[156] O. Muller, G.P. 330,832; *J.*, 1921, 429A.

[157] H. Fritzsche and Soc. of Chem. Ind. in Basle, U.S.P. 1,362,936; *J.*, 1921, 464A.

[158] Brotherton and Co. and R. W. Merriman, E.P. 155,410; *J.*, 1921, 75A.

[159] W. M. Ralph and National Aniline and Chemical Co., U.S.P. 1,371,979; *J.*, 1921, 294A, 731A.

Disazo dyes are obtained by coupling 1 mol. of 5.5′-dihydroxy-2.2′-dinaphthylamine-7.7′-disulphonic acid with 1 or 2 mols. of diazo-compounds of amines containing a sulphonic or carboxyl group in the *o*-position, *e.g.*, anthranilic acid or 4-chloro-2-amino-benzoic acid, or with 1 mol. of these diazo compounds and 1 mol. of a suitable diazo-compound; the products give on cotton pure red, bluish red to blue shades fast to ironing, after-treatment with copper salts giving bluish-red to violet shades fast to ironing and to light.[160]

Disazo dyes, giving vivid scarlet shades fast to light, washing, and fulling from an acid bath on wool, are produced by coupling tetrazotised 4.4′-diaminobenzophenone with 1 mol. of β-naphthylamine-3.6-disulphonic acid and 1 mol. of β-naphthol.[161] Similar shades are obtained by using 2 mols. of 2.6- or 2.7-naphtholsulphonic acid.[162]

Disazo dyes giving on wool in an acid bath scarlet shades fast to washing, milling, and light, are produced by combining tetrazotised 4.4′-diaminobenzophenone with 1 mol. of β-naphthol and 1 mol. of a naphtholdisulphonic acid.[163]

Direct trisazo dyes for cotton, giving greenish-blue shades fast to light and on after-treatment with formaldehyde fast to washing, are obtained by coupling diazotised 1-monoacidylamino-4-amino-naphthalene-6- or 7-sulphonic acid with 1-aminonaphthalene-6- or 7-sulphonic acid, diazotising the product, coupling with β-naphthol or 2.7-dihydroxynaphthalene, hydrolysing the acidyl group, and finally diazotising and coupling with resorcinol.[164]

A novel method for the production of azo dyes in substance is claimed to give improved results in respect to purity, strength, and depth of colour, the amine being diazotised in presence of a starch paste.[165]

Pigment Azo Dyes.

An alkali salt of the dye obtained by coupling diazotised *p*-nitro-*o*-toluidine with 2-naphthol-3.6-disulphonic acid is converted into an insoluble scarlet barium lake, which is fast to light.[166]

Scarlet lakes of remarkable fastness to light, much superior to similar colours of the Ponceau class, are obtained by combining *m*-xylidinesulphonic acid ($CH_3 : CH_3 : NH_2 : SO_3H = 1 : 3 : 4 : 5$)

[160] Farbenfabr. vorm. F. Bayer u. Co., E. P. 144,310; *J.*, 1921, 688A.
[161] Badische Anilin- u. Soda-Fabrik, G. P. 338,683; *J.*, 1921, 688A.
[162] Badische Anilin- u. Soda-Fabrik, G. P. 333,077; *J.*, 1921, 381A.
[163] Badische Anilin- u. Soda-Fabrik, G. P. 330,824; *J.*, 1921, 294A.
[164] Farbenfabr. vorm. F. Bayer u. Co., G. P. 339,183; *J.*, 1921, 731A.
[165] J. L. Kane, E. P. 164,488; *J.*, 1921, 539A.
[166] A. Linz, and Ultro Chemical Corp., U.S.P. 1,358,007; *J.*, 1921, 228A.

with R-salt, the products from other naphtholsulphonic acids not being so fast to light.[167]

The use of complex acids containing tungsten has been suggested in producing lakes.[168]

Disazo pigment dyes are obtained by coupling tetrazotised tolidine with β-naphthol-6- and -8-sulphonic acids.[169]

Triphenylmethane Dyes.

Pure greenish-blue triphenylmethane dyes, superior in fastness to light to known dyes of similar shade, are produced by heating with ethyl alcohol and a small amount of sulphuric acid a mono-alkyl-*o*-toluidine, such as the monomethyl derivative, and 2.4-dichloro-5-nitrobenzaldehyde or 2.4.5-trichlorobenzaldehyde, with subsequent oxidation of the leuco-compound.[170]

The electrolytic oxidation of the leuco-base of Malachite Green is best carried out in presence of uranyl sulphate as catalyst, when a yield of over 57% is obtained.[171]

Basic dyes are obtained by condensing acetylene with aromatic amines in presence of sulphur, followed by oxidation; aniline yields dithio-oxanilide, $C_6H_5.NH.CS.CS.NH.C_6H_5$, whereas dimethylaniline yields a compound $C_{20}H_{20}N_2S$ and finally a compound of probable constitution

$$C[C_6H_4.N(CH_3)_2]_3.C[C_6H_4.N(CH_3)_2]_3$$

which is readily oxidised by air to Methyl Violet; similarly Victoria Blue was obtained from phenyl-α-naphthylamine.[172]

Condensation of 1 mol. of benzaldehyde-*o*-sulphonic acid with 2 mols. of *o*-cresol by means of 70% sulphuric acid gives a triphenylmethane compound, $[C_6H_3(OH)(CH_3)]_2.CH.C_6H_4.SO_3H$, which on nitration gives mono- and dinitro-derivatives dyeing chromed wool from an acid bath yellowish-brown shades not fast to light or milling.[173]

[167] British Dyestuffs Corp., Ltd., J. Baddiley, and J. Hill, E.P. 164,053; *J.*, 1921, 504A.

[168] A. Lendle, and Kuttroff, Pickhardt and Co., U.S.P. 1,378,418; *J.*, 1921, 576A. A. Linz, and The Chemical Foundation, Inc., U.S.P. 1,378,882; *J.*, 1921, 539A.

[169] A. J. Field, U.S.P. 1,383,710; *J.*, 1921, 619A.

[170] British Dyestuffs Corporation, Ltd., W. H. Perkin, and G. R. Clemo, E.P. 165,658; *J.*, 1921, 576A.

[171] A. Lowy and E. H. Haux, *Trans. Amer. Electrochem. Soc.*, 1921, 99; *J.*, 1921, 730A.

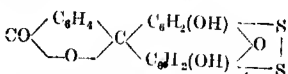
[172] F. Consonno and A. Cruto, *Gazz. Chim. Ital.*, 1921, **51**, I., 177; *J.*, 1921, 538A.

[173] P. Demont, *Rev. Gén. Mat. Col.*, 1920, **24**, 65; *J.*, 1921, 143A.

Carbazole Blue, obtained by fusing carbazole with oxalic acid, has been shown to be a tricarbazylmethane colouring matter of formula, $(C_{12}H_8NH)_2C : C_{12}H_7NH.CO_2H$, and it is assumed that the methane carbon atom is linked to each carbazole nucleus at the *p*-position with respect to the nitrogen atom. Similar to the triphenylmethane dyes, Carbazole Blue yields a carbinol which gives variously coloured salts; the corresponding tricarbazylmethane has been prepared by reduction. Carbazole Violet, obtained by fusing 9-ethylcarbazole with oxalic acid, also gives a carbinol and the parent hydrocarbon has been prepared. Both Carbazole Blue and Carbazole Violet may be sulphonated to give soluble dyes, the presence of a phenylene group exerting the same influence as the benzyl and phenyl groups.[174]

Phthalein Dyes.

An improved method for the production of thiofluorescein, or fluorescein disulphide,



which is an orange-brown acid dye, much faster than fluorescein, has been described, giving a 94% yield, by sulphurising in presence of free alkali, which opens the pyrone ring in the fluorescein. Thiogallein is the corresponding dimercaptan of fluorescein, and is a powerful mordant dye which is dyed from a neutral or acid bath in presence of hydrosulphite to prevent oxidation during dyeing, giving deeper and faster shades than gallein, increased in depth and fastness by after-treatment with copper.[175]

Carbazine Dyes.

New syntheses of carbazine dyes have been effected by the following reactions :—

$$(NO_2)_3C_6H_2Cl + H_2N.C_6H_4.CHR_2 \rightarrow (NO_2)_3C_6H_2.NH.C_6H_4.CHR_2$$
$$\rightarrow (NO_2)_2C_6H\left\langle\begin{matrix}NH\\CR_2\end{matrix}\right\rangle C_6H_4$$

in which R is an aromatic group; for example, picryl chloride and *o*-aminotriphenylmethane give the product, $C_{25}H_{18}N_4O_6$, of which the potassium derivative is converted into 2.4-dinitrodiphenylcarbazine on boiling in quinoline solution.[176]

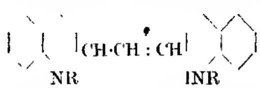
[174] M. Copisarow, *Chem. Soc. Trans.*, 1920, **117**, 1542; *J*, 1921, 41A.
[175] T. Maki, *J. Coll. Eng., Tokyo*, 1920, **11**, 1; *J.*, 1921, 143A.
[176] F. Kehrmann, M. Ramm, and C. Schmajewski, *Helv. Chim. Acta* 1921, **4**, 538; *J.*, 1921, 539A.

Pyrazolone Dyes.

A careful investigation has been made of methods for preparing Tartrazine and similar dyes in a state of purity.[177] The *m*-sulphophenylhydrazone of 1-*m*-sulphophenyl-3-carboxy-5-pyrazolone, isomeric with ordinary Tartrazine, is obtained by the condensation of 2 mols. of phenylhydrazine-*m*-sulphonic acid with 1 mol. of sodium dioxytartrate. Similarly 1.4-naphthylhydrazinesulphonic acid and the 1.5-isomer have been converted into Tartrazines. On wool and silk, the Tartrazine from phenylhydrazine-*m*-sulphonic acid gives a yellower shade than ordinary Tartrazine: the dye from the 1.4-acid mentioned gives a brighter red shade than the product from the 1.5-isomer, which is browner in tint.

Cyanine Dyes.

The work of Mills and Wishart,[178] and of Mills and Evans[179] has been confirmed[180] by examining the absorption curve in the ultra-violet of a solution of *p*-dimethylaminocinnamylidene-quinaldine methoperchlorate decolorised by hydrochloric acid, which differed very materially from that of a similar solution of isocyanine; the latter cannot therefore have the butadiene structure as stated by König.[181] The structural formula advanced by O. Fischer[182] for the carbocyanines contains one carbon atom less than is indicated by analysis, and their formulation as dimethyl derivatives of true cyanines by Wise, Adam, Stewart, and Lund[183] is not in accordance with their sensitising action or with their behaviour on oxidation. The most probable structure of the carbocyanines is considered to be :—



In the blue-sensitising dye Pinacyanol,[184] R is an ethyl group.[185] Isocyanine dyes similar to, but not identical with, those given by the corresponding derivatives of quinaldine, are obtained by treating quaternary addition compounds of pure lepidine or its homologues with alcoholic alkalis in hot, concentrated solution.

[177] M. Johnson, *J.*, 1921, 176T.

[178] *J.*, 1920, 540A.

[179] *J.*, 1920, 685A.

[180] W. König and O. Treichel, *J. prakt. Chem.*, 1921, **102**, 63; *J.*, 1921, 653A.

[181] *J. prakt. Chem.*, 1912, **86**, 166.

[182] *J.*, 1919, 199A.

[183] *J.*, 1919, 456A.

[184] E. P. 16,227 of 1905; *J.*, 1906, 368.

[185] W. H. Mills and F. M. Hamer, *Chem. Soc. Trans.*, 1920, **117**, 1550; *J.*, 1921, 41A.

The isocyanine from lepidine ethiodide resembles that from quinaldine in its photosensitising properties, and is probably isomeric.[186] The dyes obtained from the higher alkyl halides of lepidine give sensitiveness in the infra-red.[187]

The quinocyanine, 4.4′-diphenyl-ψ-isocyanine, identical with the red dyestuff produced by treatment of the ψ-base in ethereal solution with air and carbon dioxide,[188] has now been obtained by the action of 4-phenylquinolyl methiodide on the ψ-base of 2-methyl-4-quinolyl methiodide. The parent ψ-isocyanine is prepared by the addition of excess caustic potash to a solution of 2-iodoquinolyl methiodide and quinaldyl methiodide in hydrochloric acid.[189]

A new series of photosensitising dyes, "Kryptocyanines," or "K III.," are prepared by dissolving lepidine ethiodide in boiling alcohol and gradually adding a solution of sodium ethoxide and formaldehyde, with exclusion of air, when a purple-black dye is produced.[190]

Various Dyes.

Dyes are obtained by condensing a tetrahalogenated methane with a derivative of α-naphthol, in which position 4 is not substituted, in presence of an alkaline condensing agent and a catalyst.[191]

Yellow dyes, giving level shades fast to light on wool, are produced by condensing ethylenediamine with *o*-nitrohalogenbenzene-*p*-sulphonic (or carboxylic) acids, or their derivatives; for example, 2-nitro-1-chlorobenzene-4-sulphonic acid gives a product

$$(1)\,SO_3H.C_6H_3(3)NO_2(4)NH.CH_2.CH_2.NH(4).NO_2(3).C_6H_3.SO_3H(1)$$

which is also suitable for producing colour lakes, and the dye from the corresponding carboxylic acid dyes paper yellow shades fast to light.[192]

The leuco-base of Furol Green has been prepared in 30% yield by condensing furfural with dimethylaniline in presence of zinc chloride; lead peroxide converts it into the dye, which dyes silk, cellulose, and wool a brilliant yellowish-green, of only slight fastness

[186] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2389; *J.*, 1921, 75A. Also U.S.P. 1,374,871; *J.*, 1921, 413A.

[187] E. Q. Adams and H. L. Haller, U.S.P. 1,374,872; *J.*, 1921, 413A.

[188] *J.*, 1919, 199A.

[189] O. Fischer and G. Scheibe, *J. prakt. Chem.*, 1919, **100**, 86; *J.*, 1921, 11A.

[190] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661; *J.*, 1921, 75A.

[191] G. de Montmollin, H. J. Spieler, and Society of Chemical Industry in Basle, U.S.P. 1,387,596; *J.*, 1921, 731A.

[192] Badische Anilin- u. Soda-Fabrik, G. P. 336,629; *J.*, 1921, 576A.

to light in the case of wool. Diethylaniline gives "Furol Green Ae."[193]

Condensation products of the indophenol type are obtained by treating *p*-nitrosophenol, *p*-nitroso-*o*-cresol, or *p*-nitroso-*o*-chlorophenol with a phenol alkyl ether which is not substituted in the *para*-position to the alkoxy-group (*e.g.*, anisole, *o*-chloroanisole, phenetole, *o*-cresol ethyl ether, or resorcinol dimethyl ether) in presence of sulphuric acid (sp. gr. 1·71) or concentrated hydrochloric acid; the products yield leuco-compounds with sodium sulphide solution.[194]

A number of dyestuffs derived from phenanthraquinone have been prepared. Phenanthraphenazine dyes with auxochromes in the phenanthrene nucleus are prepared by condensing the corresponding amino derivatives of phenanthraquinone with *o*-phenylenediamine; the products are yellow and dye light shades on wool. The product from 2.7-diaminophenanthraquinone and 7.8-diamino-1-naphthol-3-sulphonic acid dyes fast yellow shades on wool. A number of azo dyes have been prepared; the 2.7-phenanthraquinone derivatives are good direct cotton dyes, whereas the 4.5-derivatives are good wool dyes with little affinity for cotton.[195]

Anthracene Dyes.

N-Dihydro-1.2.2′.1′-anthraquinone-azine (indanthrene) or its derivatives are obtained in improved yield and quality by fusing 2-aminoanthraquinone or its derivatives respectively with caustic potash in presence of a salt of an organic acid with which it is miscible in the fused state, such as potassium formate or acetate or a mixture of the two; a further improvement is to introduce suitable oxidising agents, such as potassium chlorate.[196] The use of a non-hydroxylic solvent, such as aniline, naphthalene, or liquid paraffin, in presence of an oxidising agent is claimed to give pure indanthrene.[197]

A further method for the chlorination of N-dihydro-1.2.2′.1′-anthraquinone-azine has been described, by treatment with sulphuryl chloride at 50°–100° C. in the presence of nitrobenzene.[198]

On heating alizarin with aniline and stannous chloride, phenylaminococramidonine is formed; similar compounds are obtained using *p*-toluidine etc., together with other hydroxy derivatives

[193] O. Fischer and L. Grahl, *J. prakt. Chem.*, 1920, **100**, 159; *J.*, 1921, 41A.

[194] Akt.-Ges. f. Anilin-Fabr., G.P. 333,897; *J.*, 1921, 342A.

[195] E. R. Watson and S. Dutt, *Chem. Soc. Trans.*, 1921, **119**, 1211; *J.*, 1921, 687A.

[196] W. J. Pope and Scottish Dyes, Ltd., E.P. 162,687; *J.*, 1921, 464A.

[197] F. W. Atack and J. Anderson, E.P. 166,297; *J.*, 1921, 619A.

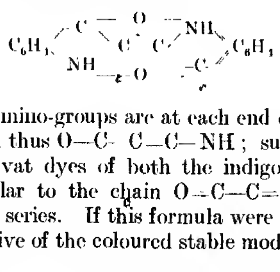
[198] Farbw. vorm. Meister, Lucius, u. Brüning, G.P. 331,283; *J.*, 1921, 294A.

of alizarin (except Alizarin Bordeaux), and their sulphonic acid dye unmordanted wool in red, violet, and blue shades.[199]

Indigoid Dyes.

The constitution of indigotin has been expressed in a new partia valency formula which is considered to symbolise the propertie and relations of chemical individuals more accurately than expres sions involving normal valencies only: colour intensification b auxochromes is attributed to the making and breaking of partia valencies. The analogy between indigotin and indanthrene i considered, and it is shown that the cause of the colour probabl resides in the interaction of the nitrogen atoms and the oxyge atoms of the quinone groups by considering the variations cause in each series by exchanging S and O for one or both NH groups.[20

Baeyer's formula for indigotin has been examined criticall in relation to the chemical behaviour and physical properties (indigotin and the known facts regarding the relation between colou and chemical constitution, and the following formula is considere more correctly to interpret the facts:—



The carbonyl and imino-groups are at each end of a five-membere conjugated system, thus O—C- C—C—NH; such an arrangemen is found in other vat dyes of both the indigoid and anthracen series, and is similar to the chain O=C—C=C—OH present i dyes of the alizarin series. If this formula were accepted, indigoti would be a derivative of the coloured stable modification of dibenz oylethylene.[201]

General rules have been formulated which predict the increas in the depth of colour in passing from brown-red isoindigo to violet red indirubin and blue indigo, the existence of a similar relationshi in the case of oxindigo, thioindigo, and indigo, and the diminutio in the depth of colour produced by substituents, such as methyl hydroxy, and amino groups and the halogens in the 6.6′-positions The union of an auxochrome and a chromophor by means of a chai of conjugated double bonds leads to an increase in the depth o colour (bathochromic effect), as in indigo, whereas the direct unio of a chromophor and an auxochrome decreases the depth of colou (hypsochromic effect), as in isoindigo; indirubin occupies a intermediate position. The bathochromic effect in passing fron

[199] Badische Anilin- u. Soda-Fabrik, G.P. 330,572; *J.*, 1921, 429A.

[200] R. Robinson, *J. Soc. Dyers and Col.*, 1921, **37**, 77; *J.*, 1921, 254A.

[201] W. Madelung, *Z. angew. Chem.*, 1921, **34**, 482; *J.*, 1921, 730A.

oxindigo to thioindigo to indigo is due to the increasing power of the auxochromes present. The effect of two auxochromes is cumulative when in *p*-position, but they act in contrary directions when in *m*-position; thus all 5.5′-derivatives in the indigoid series are deeper in colour than the corresponding 6.6′-derivatives.[202]

A series of halogenated indigos has been described, prepared by treating with acetone and alkali substituted *o*-nitrobenzaldehydes obtained by nitration of products derived from 3.5-dibromo-4-aminobenzaldehyde by replacement of the amino-groups.[203]

Isatin has been synthesised by condensing aniline with chloraloxime in acid solution, and warming the resulting isonitrosoacetanilide with sulphuric acid; similarly *p*-chloro-*o*-anisidine hydrochloride gives 4-chloro-7-methoxyisatin, which yields with indoxyl 4-chloro-7-methoxyindirubin, a compound which changes in hydrosulphite vat almost completely into ordinary indigo.[204]

Isatin-5-sulphonic acid, identical with the product of oxidation of sodium indigo-5.5′-disuphonate, is obtained by sulphonation with 20% oleum: the potassium salt condenses with indoxyl in acetic acid solution to give indirubin, which dyes wool and silk a violet shade from an acid bath.[205]

Indigoid dyes are obtained by condensing halogenated derivatives of isatin or naphthisatin, capable of reacting in the *a*-position, with 1-hydroxy-6-naphthol ethers or their derivatives not substituted in the *o*-position to the *a*-hydroxyl group; the dyes produced may be further halogenated. For example, dichloroisatin-*a*-chloride and dibromo-*β*-naphthisatin-*a*-chloride give on condensation with 6-methoxy-1-naphthol products which dye grey and olive-green shades respectively; on halogenation, the former gives a product which dyes black shades.[206] In place of 1-hydroxy-6-naphthol ethers, 1.6-dihydroxynaphthalene, or its derivatives not substituted in the *o*-position to the *a*-hydroxyl group, may be used; the products are alkylated, and may be further halogenated to give dyes identical with those described in the main patent.[207]

Methyl-6-indole-3-indole-2-indigo has been prepared from 6-methylisatin, and dyes wool and silk, but only has a slight affinity for cotton. The necessary intermediate was obtained by condensing *m*-toluidine with mesoxalic esters, and saponifying the esters of 6-methyldioxindole-3-carboxylic acid in presence of air, afterwards acidifying the alkali isatate; alternatively, *m*-toluidine reacts with

[202] J. Martinet, *Rev. Gén. Mat. Col.*, 1921, **25**, 17; *J.*, 1921, 210A.

[203] L. C. Janse, *Rec. Trav. Chim.*, 1921, **40**, 285; *J.*, 1921, 341A.

[204] J. Martinet and P. Coisset, *Comptes rend.*, 1921, **172**, 1234; *J.*, 1921, 428A.

[205] J. Martinet and O. Dornier, *Comptes rend.*, 1921, **172**, 330; *J.*, 1921, 174A.

[206] Farbenfabr. vorm. F. Bayer u. Co., G.P. 298,098; *J.*, 1921, 294A.

[207] Farbenfabr. vorm. F. Bayer u. Co., G.P. 336,211; *J.*, 1921, 576A.

carbon bisulphide in presence of hydrogen peroxide to give di-*m*-tolylthiourea, which is treated with potassium cyanide and lead carbonate in aqueous alcohol to yield hydrocyanodi-*m*-tolylcarbon-di-imide, $CH_3.C_6H_4.NH.C(.C:N):N.C_6H_4.CH_3$, and this, on heatng with aluminium chloride in benzene gives 6-methylisatin-*m*-toluide, easily hydrolysed to 6-methylisatin.[208]

N-Substituted oxindols have been prepared by heating N-mono-halogenacetyl derivatives of secondary alkylarylamines, or of diarylamines, of the general formula $N(R)(R_1).CO.CH_2.X$ (R= alkyl or aryl, R_1—aryl, X—halogen) in presence of an aluminium halide; N-phenyloxindole is obtained from chloroacetyldiphenyl-amine, and on treatment with oxidising agents, such as nitrosodi-methylaniline, yields diphenylisoindigotin.[209]

Details of a modification of the permanganate method for the estimation of indigotin have been published.[210]

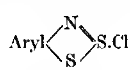
The importance of obtaining indigo and other vat dyes in a finely-divided form for working in the vat is well-recognised, and a novel method is described in which the dye is separated from solutions of the leuco-compound in presence of salts of bile acids; on blowing air through a solution of sodium-indoxyl containing 5–10% of sodium cholate, indigo separates in a very fine state of division.[211]

Sulphide dyes.

A yellow sulphide dye is obtained by heating a mixture of 5-aminocymene, *m*-toluylenediamine, and sulphur, whereas a green dye results on heating a mixture of acetaminocymene, a *p*-amino-hydroxy-aromatic compound, and sulphur.[212]

Indophenols have been prepared by oxidising equimolecular proportions of tetrahydro-*a*-naphthylamine or its mono- or dialkyl-amino-derivatives and *p*-aminophenol or its substitution products, and are used for the production of fast blue sulphide dyes.[213]

Products having the general constitution



are formed by the action of sulphur monochloride on the dry salts of aromatic amines in which one *o*-position to the amino-group is free, or, preferably in presence of a diluent such as benzene

[208] J. Bonnefoy and J. Martinet, *Comptes rend.*, 1921, **172** 220; *J.*, 1921, 174A.

[209] R. Stollé, G.P. 335,763; *J.*, 1921, 503A.

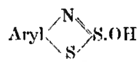
[210] W. Thomson, *J. Soc. Dyers and Col.*, 1921, **37**, 166; *J.*, 1921, 464A.

[211] C. H. Boehringer Sohn, G.P. 326,573; *J.*, 1921, 210A.

[212] C. E. Andrews, and The Selden Co., U.S.P. 1,314,928-9; *J.*, 1921, 294A.

[213] Farbenfabr. vorm. F. Bayer u. Co., G.P. 338,817; *J.*, 1921, 731A.

or naphtha, on the free bases or their aryl derivatives; chlorination also occurs in *p*-position to the amino-group when that position is free or substituted by an atom or group which is easily replaced by chlorine. On treatment with aromatic bases, most of these products yield red, violet to blue basic dyes, but with bases containing an alkyl group in *p*-position to the amino group, *e.g.*, *p*-toluidine or *m*-xylidine, sulphide dyes are formed giving yellow to brown shades fast to chlorine on cotton; the active chlorine atom still present in the latter products condenses with aromatic bases, giving yellow to orange sulphide dyes.[214] On treatment with water, the initial products just described give ring compounds of the general formula



the ring of which is opened by treatment with alkalis, preferably with addition of a reducing agent, *e.g.*, hydrosulphite, giving with monochloroacetic acid aromatic *o*-aminocarboxylic acids; the latter are diazotised and converted into the nitriles, which, after saponification, may be transformed into new ring compounds yielding leuco vat dyestuffs by warming with dilute acids. The products are distinguished from known thioindigo dyestuffs by the brilliancy of their shade, their greater affinity for the fibre, and their increased fastness to washing, scouring, acid cross-dyeing, and bowking.[215]

Vat Dyes of Unknown Constitution.

Valuable bluish-grey to greenish-grey vat dyes are obtained by heating with a saturated alcoholic solution of ammonium sulphide the *m*- or *p*-nitroanilides of benzoquinone, or more especially of halogenated benzoquinones.[216]

The condensation of benzidine with chloroacetic acid, with or without addition of alkalis, yields a glycine which on fusion with caustic alkalis with addition of suitable condensing agents gives a vat dye which dyes cotton and wool blue-green shades; esters of chloroacetic acid may be used, with saponification of the glycine if necessary.[217]

On heating *a*-naphthoquinone with water under pressure, in addition to *a*-naphthoquinol a yellow condensation product results which on reduction yields green vat and pigment dyestuffs; the latter is obtained directly by boiling *a*-naphthoquinone with phenol, water being added to maintain a b.p. of about 120° C. On reduction with zinc dust in concentrated sulphuric acid solution, the insoluble

[214] L. Cassella u. Co., E.P. 17,417 of 1914; *J.*, 1921, 619A.

[215] L. Cassella u. Co., E.P. 18,292 of 1914; *J.*, 1921, 619A.

[216] L. Cassella u. Co., E.P. 147,703; *J.*, 1921, 688A.

[217] Chem. Fabr. vorm. Weiler-ter Meer, G.P. 300,094; *J.*, 1921, 464A.

green pigment dye is obtained by pouring into ice-water, and may be used as a vat or sulphide dye for dyeing and printing wool and cotton.[218]

Natural Dyes.

The conditions affecting the quality of the Java indigo plant have been investigated, and the richness of the leaf in indigotin has been materially increased by using a soil of low nitrogen content[219]; the same author has suggested the development of the indigo industry in Assam in conjunction with tea or flax crops.[220]

The work of Shibata and others[221] on the anthocyanins and anthocyanidins has been criticised, and further evidence has been obtained in support of the view that in nature yellow sap pigments of the flavonol group are first formed and the anthocyan colouring matters are then produced from them by reduction.[222]

Melanin, the pigment of the skin of the Australian black, contains about 50% of carbon and is free from iron; it resembles the pigment obtained[223] from the wool of the black sheep.[224]

[218] Badische Anilin- u. Soda-Fabrik, E.P. 168,447; *J.*, 1921, 730A.

[219] W. A. Davis, *Agric. Res. Inst. Pusa, Indigo Publ. No.* 7; *J.*, 1921, 173A.

[220] W. A. Davis, *ibid.*, *Publ. No.* 8; *J.*, 1921, 127R.

[221] *J.*, 1919, 217A.

[222] A. E. Everest and A. J. Hall, *Proc. Roy. Soc.*, 1921, **92B**, 150; *J.*, 1921, 381A.

[223] Gortner, *J.*, 1910, 1298.

[224] W. J. Young, *Biochem. J.*, 1921, **15**, 118; *J.*, 1921, 504A.

FIBRES, TEXTILES, CELLULOSE, AND PAPER.

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Much excellent work has been carried out during the past year in the realms of pure science, and many of the results obtained will be of indirect benefit to industry, but unfortunately the direct application of science to industry does not appear to have received an equal share of attention. It is, however, gratifying to note that the several Research Associations have now commenced their activities. The literature connected with the science and technology of textiles is notoriously chaotic, and one of their first functions will, doubtless, be to collect and prepare systematic reviews of the more important parts. It is to be hoped that steps will be taken to secure the general publication of such collections of information, which would be of immense value to workers in the fields of both pure and applied research.

Cotton.

Little work of outstanding importance, relevant to the physical and chemical properties of cotton, apart from cellulose, has been published during the year. It is gratifying to note, however, that problems affecting its cultivation are receiving the attention of scientists and much information has been amassed concerning the economic production of cotton in various parts of the world. Abstracts of the most important articles appearing in this connexion (which does not come within the scope of this review) will be found in the *Journal of the Textile Institute*.

The organisation in this country of the various Associations connected with the growing of, and research on, cotton, is apparently arousing interest in America,[1] where the formation of similar organisations is recorded. The aims of the Preliminary Committee on American Cotton Research are dealt with by D. E. Douty,[2] and the projected scheme of work of the Cotton Research Co., Inc., of Boston, Mass., is discussed by G. H. Goldsmith.[3]

[1] *Text. World J.*, 1920, **58**, 41.
[2] *Ibid.*, 1921, **59**, 869.
[3] *Ibid.*, 1921, **59**, 871, 939, 943.

The Information Bureau of the British Cotton Industry Research Association has published a bi-monthly summary of current literature during the year, which contains an extensive collection of admirably-arranged abstracts on all subjects bearing on the science and technology of cotton. Unfortunately, they are not at present available for general circulation, but it is to be hoped that steps will be taken to secure the publication of collected abstracts, which will be of immense value to workers not directly connected with the cotton industry.

In an article on the classification of cottons, W. Hacker[4] deals briefly with the general physical characteristics such as "feel," and length of staple of 54 varieties of cotton. W. Robinson,[5] in the course of an article on the microscopic markings on flax and other vegetable fibres, attributes their absence in the cotton fibre to structural differences in the cell wall of the cotton hair, which is probably more elastic than that of fibres of the flax type.

A useful method for the cutting of microtome sections of cotton fibres, yarns and fabrics has been developed by R. S. Willows and A. C. Alexander,[6] who employ a simple method of cellulose ester-paraffin wax embedding. The use of agar as an adhesive in place of albumin for the cementing of sections to the microscope slide is suggested. H. J. Denham[7] suggests a modification of Breckner's embedding process for the cutting of sections of cotton hairs. The relation between the constituents of the raw cotton fibre and the efficiency of the boiling-out and bleaching processes through which the woven fabric passes are discussed by J. Merritt Mathews.[8]

M. Freiberger[9] has correlated the amounts of water, ash, wax, and nitrogenous matter, etc. present in American cotton, Maco cotton, and desized cotton fabric, but gives no details of the analytical methods employed.

A, Scheurer,[10] in examining the hygrometric properties of fibres, finds that there is a maximum "absorbing capacity" for cotton, amounting to about 20% of water, attainable when bleached cotton in placed in an atmosphere saturated with water, irrespective of temperature. It is stated that cotton, wool, and silk, when exposed to air of the same moisture content, take up water in amounts proportional to their maximum absorptive capacities. Experiments bearing on the constitution of cotton cellulose have been made by F. Lenze, B. Pleus, and J. Mueller,[11] who consider

[4] *Text. Zeit.*, 1921, **52**, 269.
[5] *J. Textile Inst.*, 1921, **12**, 339.
[6] *Ibid.*, 1921, **12**, 99; *J.*, 1921, 294A.
[7] *Nature*, 1921, **107**, 299.
[8] *Text. Manuf.*, 1921, **47**, 87.
[9] *Textilber.*, 1921, **2**, 345.
[10] *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 129.
[11] *J. prakt. Chem.*, 1920, **101**, 213.

material suitably treated with alkali to be free from xylose residues, and R. Prosiegel,[12] who has studied its acetolytic decomposition.

In continuation of previous work E. Knecht,[13] in collaboration with F. P. Thompson, has examined the effect of acids on cotton, boiling the material with dilute sulphuric and hydrochloric acids. He finds that by this treatment its tensile strength and affinity for methylene blue are decreased, but on drying amounts of sulphuric acid in the fabric, a marked increase in the affinity for methylene blue and rhodamine-B was noted.

M. Nakano[14] has found that when cotton cellulose is heated in air, or mercerised, the viscosity of its solutions in cuprammonium is reduced in proportion to the elevation in temperature or to the increase in concentration of the alkali.

The report by R. A. Punter[15] on the industrial applications of researches on the viscosity of cotton cellulose is reviewed later. N. Fleming and A. C. Thaysen,[16] extending their researches on the bacterial deterioration of cotton during storage, have devised a method of quantitatively determining the bacterial degradation of fibres by utilising the viscose treatment as a swelling agent. They find that Indian cottons deteriorate much more rapidly than American cottons or cotton grown in India from American seed. The observations of C. Dorée,[17] who has investigated the tendering action of sea-water on cotton fabrics, are dealt with under the section on Textile Fabrics.

Wool.

The amount of published material coming within the province of this section of the report is very small, and no progress appears to have been made during the year in the investigation of the chemical constituents of wool and other animal fibres. A voluminous amount of work on their physical and other properties, in so far as they affect manufacturing processes, still remains to be cleared up.

The organisation of the British Research Association for the Woollen and Worsted Industries, and the equipment of their laboratories, now appears to be almost complete. In a review of their first Annual Report,[18] it is stated that a number of investigations of technical importance have been published and details of a projected scheme of researches are outlined.

[12] *Zellstoffchem. Abhandlungen*, 1920, **1**, 6, 25.

[13] *J. Soc. Dyers and Col.*, 1921, **37**, 270.

[14] *Kōgyō-Kwagaku Zasshi*, 1921, **24**, 918; *J.*, 1921, 807A.

[15] *J.*, 1920, 333T.

[16] *Biochem. J.*, 1921, **15**, 406; *J.*, 1921, 764A.

[17] *Biochem. J.*, 1920, **14**, 709; *J.*, 1921, 342A.

[18] *J. Textile Inst.*, 1921, **12**, 70.

R. O. Herzog and W. Jancke[19] have applied X-ray spectrographic methods of examination to the wool fibre and find it to be completely amorphous.

The hygrometric properties of wool are the subject of examination in a research by A. Scheurer,[20] who has investigated the amounts of water taken up by various textile fibres from moist air. He finds that wool, like cotton, has a maximum absorbing capacity for water when exposed to air saturated with water vapour, being capable of taking up 34% of water, and that when dried it regains moisture in an amount proportional to this constant.

R. Reychler[21] finds that, on heating wool under conditions of normal or increased pressure with water, alkaline or acid solutions, acid or basic substances are dissolved, which are capable of reacting with basic or acid dyes. The physical properties of the fibre are altered as indicated by loss of double refraction, diminution of elasticity, and increase of plasticity.

The subject of the scouring of wool has received only little attention. H. Hey[22] has outlined the principles of the degreasing of wool by volatile solvents, and J. P. Craven[23] has contributed an interesting article on the employment of the solvent degreasing process in the United States. The use of chlorinated hydrocarbons of the aliphatic series as degreasing agents is protected by F. Koch.[24]

The action of acids on wool has been examined by M. Becke,[25] who states that after treatment with acid solutions, wool acquires an acidic character, and its resistance to alkalis is diminished. He has investigated the action of sulphuric, oxalic, formic, and acetic acids, finding that the amount of wool dissolved by solutions of sulphuric acid, and on subsequent treatment of the residual material with sodium carbonate solutions, is proportional to the acid concentration employed. In a later article he deals with the effect of acid treatment from the points of view of dyeing and carbonising.

The addition of reactive aldehydes (formaldehyde, acetaldehyde etc.), acetone, or aceto-acetic ester to carbonising mixtures to prevent the deleterious action of these agents on wool or artificial wool is the subject of a patent by M. Becke.[26] P. Heermann[27] states that the use of too strong an acid or too high a

[19] *Umschau*, 1921, **25**, 53; *J.*, 1921, 342A. *Cf. Ber.*, 1920, **53**, 2162.
[20] *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 129; *J.*, 1921, 539A.
[21] *Bull. Soc. Chim. Belg.*, 1920, **29**, 291; *J.*, 1921, 174A.
[22] *J. Soc. Dyers and Col.*, 1921, **37**, 183.
[23] *Yorkshire Observer*, Aug. 4, 1921.
[24] U.S.P. 1,358,163; *J.*, 1921, 6A.
[25] *Textilber.*, 1921, **2**, 194, 213; *J.*, 1921, 381A.
[26] G.P. 334,528; *J.*, 1921, 504A.
[27] *Textilber.*, 1921, **2**, 106; *J.*, 1921, 210A.

temperature during the carbonising process may result in the development of stains in dyeing.

L. L. Lloyd[28] points out the danger of the use of unsuitable oils as wool lubricants. C. H. Boehringer Sohn Chem. Fabr.[29] claim that the addition of salts of bile acids to the soap solution during the milling operation, greatly increases its efficiency and serves to protect the wool against the action of alkalis.

In connexion with the analysis of wool refuse, A. Demolon[30] makes suggestions concerning the technique of nitrogen determinations. An interesting series of analyses of suint and greases from typical wools has been carried out by the U.S. Bureau of Chemistry.[31]

SILK.

Little work of any material scientific or technical importance appears to have been carried out during the year on the subject of silk, and it is to be hoped that with the organisation of the silk industry and formation of the Silk Research Association, stimulus will be given to individual researchers, particularly those working in the field of bio-chemistry, to turn their attention to the many important problems connected with the structure and various properties of silk, which at present await investigation.

Questions bearing on the cultivation of and rearing of the silkworm under antiseptic conditions have received attention on the continent and in Japan. V. K. Osgian[32] claims to have achieved remarkable success in obtaining coloured silks by suitably dieting the silkworm, but expert opinion appears to be divided on the subject. An article reviewing the various authentic attempts to produce coloured silks by this method has been published recently.[33]

The structure of the silk fibre has been examined by R. O. Herzog and W. Jancke,[34] who, employing X-ray spectrographic methods, state that it is of a crystalline character.

W. Türk[35] has made a chemical examination of sericin, which he obtained by digestion of silk with water under pressure, and has found evidence of carbohydrate-protein complexes in alcohol-soluble and alcohol-insoluble sericin. Hydrolysis of alcohol-insoluble sericin with sulphuric acid gave varying amounts of tyrosine, leucine, serine, arginine, lysine, and histidine.

[28] *J. Textile Inst.*, 1921, **12**, 102.
[29] G.P. 334,575; *J.*, 1920, 779A.
[30] *Ann. Chim. Analyt.*, 1921, **3**, 244; *J.*, 1921, 688A.
[31] *Text. World J.*, 1920, **58**, 261.
[32] *Canadian Textile J.*, 1921, Aug. 4, 17.
[33] *Silk*, 1921, **14**, 41.
[34] *Chem. Zentr.*, 1921, **92**, II., 573; *J.*, 1921, 342A. *See also Ber.*, 1920, **53**, 2162.
[35] *Z. physiol. Chem.*, 1920, **111**, 71; *J.*, 1921, 126A.

Results of analyses of Japanese and Manchurian silks are given by R. Inouye, S. Iwaoka, and M. Hirusawa,[36] which, contrary to expectations, show them to be chemically identical. It is pointed out that analyses of tussah silk are invariably similar to those of true silk, with the exception of differences in the ratio of alanine to glycine.

A. Scheurer[37] has investigated the amounts of water taken up by silk under various conditions, and finds that when thoroughly dried and exposed to an atmosphere of water-saturated air, it is capable of absorbing, as a maximum amount, 29% of water.

Processes for the degumming of silk still continue to be introduced. G. Bonwitt and O. Goldschmidt[38] claim the use of neutral or feebly alkaline solutions containing peroxides (with addition of gelatinous substances if necessary) as degumming agents. The use of soap solution containing per-salt, is the subject of a subsequent patent, in this connexion, by O. Goldschmidt.[39]

L. Mayfield[40] applies a suitably adapted conditioning process to the production of soft and easily-manipulated yarns for knitting purposes.

A process for the preparatory treatment of wild silk yarns has been devised by S. Sakane,[41] who renders them workable by repeated souring and soaping.

Bast and Other Vegetable Fibres.

Our knowledge concerning the technology of the more common bast fibres, and of many of the scientific problems connected therewith, does not appear to have increased to any very appreciable extent during the year.

The retting process still occupies the attention of investigators, and new methods of retting continue to be evolved, but apart from these communications, which constitute the bulk of the published work, it is not possible to direct attention to more than one or two papers of general interest.

Y. Uyeda,[42] in continuation of earlier work on the cellulose content of bast fibres,[43] has made further experiments on the estimation of cellulose in Korean hemp, employing three different methods, and recommends Renker's modification of Cross and Bevan's chlorination process as being the most practical one for the estimation of cellulose in bast fibres from the point of view of

[36] *J. Tokyo Chem. Soc.*, 1920, **41**, 876.

[37] *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 129 ; *J.*, 1921, 539A.

[38] G.P. 335,777 ; *J.*, 1921, 504A.

[39] E.P. 131,906 ; *J.*, 1921, 175A.

[40] E.P. 159,907 ; *J.*, 1921, 295A.

[41] Japanese Pat. 36,336, 7.5.20.

[42] *J. Ind. Eng. Chem.*, 1921, **13**, 141 ; *J.*, 1921, 174A.

[43] *Ibid.*, 1920, **12**, 573 ; *Ann. Repts.*, 1920, **5**, 128.

textile chemistry. He discusses the function of pectin in bast fibres and opines that the cellulose of hemp fibre has, in some degree, an oxycellulose structure.

P. Casparis,[44] in the course of experiments on lignified cell membranes, obtained a blue coloration on treating these tissues with solutions of cobalt thiocyanate of from 15 to 40%. This reaction, which is not shown by unchanged cellulose, is supposed to be an adsorption phenomenon, and is stated to be more sensitive and reliable than the usual well-known tests for lignified matter. It seems possible that it may be of value as a means for the detection of adulterants in flax.

Efforts have been made in Germany to stimulate scientific investigation of the retting process, and in this connexion the Verband Deutscher Leinen-Industrieller e. V. of Berlin-Biefeld, offered, early in 1920[45] a number of prizes to the value of 70,000 marks for the solution of problems connected with the determination of the end-point in the retting of bast fibres, with methods for the recognition of under- and over-retted flax, technical methods for overcoming the odour of retting, purifying the effluent, and for permitting retted fibres to be dried artificially with satisfactory results.

The question of determining the completion of the retting process, with reference to the difficulties arising in ensuring its standardisation, have been subsequently discussed in the course of an interesting article.[46]

A number of experiments on the conditions affecting the retting of flax, hemp, ramie, jute, and nettles, have been made by E. Kayser and H. Delaval,[47] who, employing six different micro-organisms for the retting of sterilised material, have determined the optimum conditions for their growth, the factors affecting their development, and the nature of the products formed as the result of their action. They emphasise the fact that with proper scientific control a standardisation of the retting process might be effected.

B. S. Summers[48] proposes to regulate the retting of flax by adjustment of the oxygen absorption value of the retting liquor. L. A. Johnson[49] claims to accelerate the retting of flax by a preliminary removal of the gums and resins present in the straw, employing for the purpose a treatment with an alkaline solution prepared from "Magadi soda," a mixture of sodium carbonate and bicarbonate, of East African origin. C. R. Turner[50] proposes to remove

[44] *Pharm. Monats.*, 1920, **1**, 121, 137, 153; *J.*, 1921, 343A.

[45] *Mitt. des Forschungs-Instituts. Sorau*, 1920.

[46] *J. Dept. Agric. and Tech. Instr. for Ireland*, 1921, **21**, 248

[47] *Bull. Soc. d'Encour.*, 1920, **132**, 277; *J.*, 1921, 382A.

[48] E.P. 158,807; *J.*, 1921, 211A.

[49] E.P. 151,143; *J.*, 1920, 718A.

[50] E.P. 165,240; *J.*, 1921, 808A.

the gum-like substances remaining on bast-fibres after retting by washing the bundled material in a suitably-arranged centrifugal machine. A novel method for the production of soft fibrous materials from bast or similar fibres is patented by E. Claviez.[51] After digestion of the raw material with alkaline solutions, it is subjected to a freezing process, which breaks down the natural fibre agglutinants surviving the boiling treatment.

In continuation of work on the retting of exotic plants, P. Krais[52] finds that borax, when substituted for sodium bicarbonate, which he had previously employed to ensure an alkaline condition, retards the retting process. The experiments were primarily carried out with a species of Brazilian mallow, and subsequently extended to flax and nettles with similar results.

R. Weiss[53] gives details of an empirical process for the degumming of ramie. Casein is stated to have been used with success in removing pectoses from textile fibres.[54] The action of the substance is said to depend on the fact that when heated it evolves ammonia, which reacts with the insoluble pectoses, forming readily soluble and easily removable pectates.

The shortage of fibrous raw materials in Central Europe, and their present high cost of importation, is causing German and Austrian scientists to continue the devotion of their activities to the utilisation of other and cheaper sources of supply, and to further exploitation of their natural resources. Many new, and apparently successful substitutes for silk, wool, and cotton have been produced.

Processes for the preparation of fibres from a diversity of sources form the subject of a large number of French, German, Italian, American, and Japanese patents, which cannot be dealt with in detail. Peat is one of the particularly novel sources employed. The Aktieselskap Norsk Torvtextil[55] obtain fibrous products from this material by a process of weak acid digestion followed by an alkaline treatment.

Methods for the manufacture of "imitation" fibres, and the production of special effects on fibrous materials continue to be evolved. Gillet et Fils[56] produce wool-like effects on vegetable fibres by fixing thereon the products of hydrolysis of casein, serum albumin, and other proteic materials. K. Takani[57] obtains an artificial wool by treatment of cotton with suitably-filled rubber solutions.

[51] E.P. 163,049; *J.*, 1921, 577A.
[52] *Z. angew. Chem.*, 1920, **33**, 277; *J.*, 1920, 816A.
[53] *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 404.
[54] *L'Industrie Text.*, 1921, **37**, 190.
[55] Norwegian Pat. 30,805, 14.6.20.
[56] E.P. 150,665; *J.*, 1921, 143A.
[57] Japanese Pat. 36,395, 18.5.20.

Artificial hemp is prepared according to L. Nakagami[58] by treating borax-impregnated cotton fibre with a paste of *Hydrosme rivieri*, followed by drying and exposure to steam containing ammonia gas. S. Takasa and the Yokohama Kōgyō Co.[59] propose to manufacture imitation hemp by treatment of cotton threads with aluminium acetate, followed by drying and coating with a mixture of specially-prepared viscose, resin soap, and Turkey red oil, the coated material being subsequently steamed, washed, and dried. The product is stated to withstand washing, bleaching, and dyeing.

Artificial Silk.

There are few developments to record in connexion with artificial silk; the bulk of the current literature devoted to the subject is mainly composed of semi-popular articles. Of the patents published, only a small number present specially novel features. No progress appears to have been made with regard to methods for the manufacture of staple fibre and allied artificial products.

X-Ray examinations of the structure of various artificial silk fibres have been carried out by R. O. Herzog and W. Jancke.[60] Viscose silk is stated to retain the crystalline character of cellulose, whereas artificial silk produced from cellulose acetate was found to be amorphous.

The employment of polarimetric methods of control in the preparation of cellulose solutions for artificial silk manufacture is advocated by H. Schulz.[61] A new type of artificial fibre, "Holken" silk,[62] has been obtained from Maco cotton, and is stated to be very durable, possessing considerable strength when wet.

R. Schwarz[63] discusses the possible development of cellulose-ether artificial silk production. It is stated that if cellulose ethers could be cheaply employed in this connexion the resulting products would be superior to cuprammonium and cellulose ester silks in their water- and alkali-resisting properties, though their slight affinities for colouring matters might constitute a serious drawback to their general employment.

E. Bronnert[64] proposes to regulate the degree of fineness of the threads obtained in the spinning of viscose by adjusting the amount of acid present in the spinning bath. The minimum quantity of sulphuric acid, in grams per litre, to be used for the production of a thread of required denier, may be calculated from a formula, a

[58] Japanese Pat. 36,315, 5.5.20.
[59] Japanese Pat. 36,743, 16.7.20.
[60] *Ber.*, 1920, **53**, 2162; *cf. J.*, 1921, 342A.
[61] *Deut. Faserstoffe*, 1921, **3**, 109.
[62] *Ibid.*, 1921, **3**, 51.
[63] *Ibid.*, 1921, **3**, 28.
[64] E.P. 166,931; *J.*, 1921, 654A.

relationship being found to exist between this figure and the square root of the denier required. In other patents he gives details of the use of acid baths of various compositions.

Questions relating to the production of viscose threads have received a fair share of attention and claims for the use of a variety of coagulating agents are put forward. The employment of acidified sulphite waste lye forms the subject of one patent, and the addition of sodium benzenesulphonate figures in another.

J. C. Hartogs[65] employs an electrical treatment of the thread immediately after spinning to enhance the appearance and feel of viscose silk.

Economics in viscose silk production are claimed to be effected by making the various processes cyclic, and patents have been taken out for deodorising the gases evolved, and for the recovery of by-products during the manufacture of viscose.

Methods for the production of artificial fibres of wool- or cotton-like character have been devised by the Glanzfäden A.-G.[66] who employ a modified viscose treatment. L. Drut[67] proposes to obtain fibres of a woolly nature by emulsifying solutions used in the preparation of the various artificial silks with air or inert gases, and spinning them into a precipitating medium while in an emulsified condition.

The Glanzfäden A.-G.[68] claim to bring about alteration of the spinning properties of cuprammonium-cellulose solutions by varying the state of hydration of the cellulose in solution. They state that it is dehydrated by addition of invert and starch sugars, and hydrated when cane sugar is added. The full strength, gloss, and elasticity of the fibre are only obtained when cellulose is completely hydrated before spinning.

Yarns and Fabrics.

Sizing is one of the most important steps in the preparation of yarns for the manufacture of textile fabrics, and until recently no very serious attempts had been made to effect a thoroughly scientific standardisation and control of the process.

It is gratifying to note that new methods of sizing are being devised and that several articles dealing with those problems connected with the process, which require immediate investigation, have been published.

An interesting series of investigations on the effect of sizing cotton warps with starch mixtures of different physical properties has been carried out.[69] New machinery for the sizing of various

[65] G.P. 337,642 ; *J.*, 1921, 621A.

[66] E.P. 135,205, 152,349, 152,350, 152,351 ; *J.*, 1921, 254A, 343A.

[67] E.P. 143,253 ; *J.*, 1921, 689A.

[68] E.P. 145,035 ; G. P. 306,107 ; *J.*, 1918, 575A.

[69] *Cotton*, 1921, **85**, 481 ; *Textile World J.*, 1921, **59**, 2895.

textile materials has been introduced, and several novel methods for the preparation of size ingredients developed.

R. Huenlich[70] suggests the use of partially dextrinised potato starch as a sizing agent. Hydrogenated fish oils[71] are recommended as substitutes for the more expensive oils at present employed as softening agents in the preparation of size mixtures.

The various factors affecting the activity of amylases are discussed by W. Biedermann and A. Rucha,[72] and also by A. Desgrez and R. Hoog.[73] The Soc. Suisse des Ferments[74] patent methods for the application of animal amylases in the degumming of textile materials.

Methods for the testing of amylase solutions have been devised by E. von Euler and O. Svanberg.[75] J. L. Baker and H. F. Hulton[76] describe a process for the iodometric testing of diastase extracts.

It is to be hoped that with increase in our knowledge of enzyme chemistry, and methods for controlling the activity of enzymic preparations, many new processes for the removal of foreign matter from textile materials will be introduced.

Numerous patents dealing with the fireproofing, waterproofing, stiffening, strengthening, rendering impermeable to gases, and doping of fabrics have been published during the year but no very novel features appear. F. Moeller[77] proposes to employ thionyl chloride alone, or in presence of indifferent solvents, for the waterproofing or hardening of cellulosic materials.

An exhaustive study of the efficiency of various methods of waterproofing cotton duck has been made by F. P. Veitch and T. D. Jarrell,[78] who discuss the value of the various tests employed.

An interesting account of researches on the action of ultra-violet light on fabrics has been published by M. Entat.[79] The various precautions to be observed in carrying out comparative tests on different materials are dealt with in detail, and special consideration is given to the protective action of certain dyestuffs on fabrics. It is shown that undyed silk suffered a greater reduction in tensile strength than similar material which had been dyed, when both were exposed, under the same conditions, to a mercury vapour lamp. A "coefficient of protection" of dyed silk has been determined for each of a number of dyestuffs.

[70] *Z. ges. Textil-Ind.*, 1921, **24**, 278.
[71] *Textile Colorist*, 1921, **43**, 106.
[72] *Fermentforsch.*, 1921, **5**, 56.
[73] *Comptes rend.*, 1921, **172**, 551.
[74] E.P. 145,583; *J.*, 1921, 383A.
[75] *Z. physiol. Chem.*, 1921, **112**, 193; *J.*, 1921, 483A.
[76] *Analyst*, 1921, **46**, 90; *J.*, 1921, 272A.
[77] E.P. 145,610-1; *J.*, 1921, 842A, 843A.
[78] *J. Ind. Eng. Chem.*, 1921, **13**, 672; *J.*, 1921, 806A.
[79] *Rev. Gén. Mat. Col.*, 1920, **24**, 149.

relationship being found to exist between this figure and the square root of the denier required. In other patents he gives details of the use of acid baths of various compositions.

Questions relating to the production of viscose threads have received a fair share of attention and claims for the use of a variety of coagulating agents are put forward. The employment of acidified sulphite waste lye forms the subject of one patent, and the addition of sodium benzenesulphonate figures in another.

J. C. Hartogs[65] employs an electrical treatment of the thread immediately after spinning to enhance the appearance and feel of viscose silk.

Economics in viscose silk production are claimed to be effected by making the various processes cyclic, and patents have been taken out for deodorising the gases evolved, and for the recovery of by-products during the manufacture of viscose.

Methods for the production of artificial fibres of wool- or cotton-like character have been devised by the Glanzfäden A.-G.[66] who employ a modified viscose treatment. L. Drut[67] proposes to obtain fibres of a woolly nature by emulsifying solutions used in the preparation of the various artificial silks with air or inert gases, and spinning them into a precipitating medium while in an emulsified condition.

The Glanzfäden A.-G.[68] claim to bring about alteration of the spinning properties of cuprammonium-cellulose solutions by varying the state of hydration of the cellulose in solution. They state that it is dehydrated by addition of invert and starch sugars, and hydrated when cane sugar is added. The full strength, gloss, and elasticity of the fibre are only obtained when cellulose is completely hydrated before spinning.

Yarns and Fabrics.

Sizing is one of the most important steps in the preparation of yarns for the manufacture of textile fabrics, and until recently no very serious attempts had been made to effect a thoroughly scientific standardisation and control of the process.

It is gratifying to note that new methods of sizing are being devised and that several articles dealing with those problems connected with the process, which require immediate investigation, have been published.

An interesting series of investigations on the effect of sizing cotton warps with starch mixtures of different physical properties has been carried out.[69] New machinery for the sizing of various

[65] G.P. 337,642; *J.*, 1921, 621A.

[66] E.P. 135,205, 152,349, 152,350, 152,351; *J.*, 1921, 254A, 343A.

[67] E.P. 143,253; *J.*, 1921, 689A.

[68] E.P. 145,035; G. P. 306,107; *J.*, 1918, 575A.

[69] *Cotton*, 1921, **85**, 481; *Textile World J.*, 1921, **59**, 2895.

E. A. Fisher, in the course of a series of articles published during the year in the *Journal of the Textile Institute*, gives valuable suggestions for the interpretation and representation of quantitative experimental values, obtained in the course of textile work, which will be welcomed in this connexion.

Cellulose.

Physical and Colloid Properties.

The subject of the physical and colloid properties of cellulose in its various forms presents an almost unopened field for research, and it is to be regretted that, compared with the chemical aspect of cellulose, little advancement has been made during the year. It is probable, however, that as the industries connected with the utilisation of cellulosic materials become more organised and their demands more insistent, the attention of the physicist and physical chemist will be more definitely directed towards the elucidation of the many vital and fundamental problems, which at present await solution.

In connexion with results previously obtained by von Weimarn, F. Beck [86] has made experiments on the strength of cellulose films, and finds that films prepared from neutral salt solutions of cellulose, which are weaker than those formed from viscose and cuprammonium solution, may be increased in wet and dry tensile strength to the extent of 80%, by treatment with a concentrated calcium thiocyanate solution followed by washing and drying. In the case of films formed from calcium thiocyanate solutions of cellulose, it has been noted that the presence of a trace of solvent remaining in the film causes increased tensile strength. In a reply to these criticisms, P. P. von Weimarn [87] makes observations on methods for increasing the strength of cellulose films, and in a subsequent article,[88] points out that the swelling of cellulose by aqueous neutral salt solutions is dependent on the state of hydration of the salt in solution.

In continuation of an earlier research,[89] S. J. Lewis [90] has made further experiments on the fluorescence of cellulose in the form of paper and fabrics, and has extended the work to cellulose acetate. His method of procedure is to focus an ultraviolet spectrum on the surface of the material, which is suitably arranged in a quartz spectrograph, and to photograph the resulting "glow" by means of a special camera. The work, which is not yet complete, at present indicates that specimens of cellulose and

[86] *Z. angew. Chem.*, 1921, **34**, 113; *cf. J.*, 1921, 254A.

[87] *Kolloid Zeits.*, 1921, **29**, 197; *J.*, 1921, 842A.

[88] *Kolloid Zeits.*, 1921, **29**, 198; *J.*, 1921, 842A.

[89] *J. Soc. Dyers and Col.*, 1918, **34**, 167.

[90] *J. Soc. Dyers and Col.*, 1921, **37**, 201; *J.*, 1921, 620A.

its derivatives which from the usual considerations would be regarded as being identical, show marked differences in their fluorescent properties.

In the course of a critical review of the utility of the various methods of electrical investigation usually adopted by biologists and colloid chemists, R. Keller[91] points out the importance of dielectric constant determinations. He has investigated the dielectric constants of a number of carbohydrates, including cellulose.

An observation of immediate technical interest is made by E. Arnould,[92] who finds that the presence of small amounts of sodium chloride, adsorbed by the cellulose and not removable by washing with water, may prevent the satisfactory sizing of paper by the rosin-alum process. These impurities may, however, be satisfactorily removed by treatment of the material with dilute caustic soda solution.

A series of interesting contributions on adsorption have been made by I. M. Kolthoff.[93] In examining the amounts of sodium and potassium hydroxide taken up by cotton wool and filter paper from solutions of increasing normality, he finds that with unit weight of cellulosic material the amounts of alkali taken up increase with the end concentration of the solution up to a strength of 4*N*. Between 4*N* and 6*N* the quantity taken up is constant, but above 6*N* there is a sudden increase, followed by a constant value until the final end concentration reaches 8*N*. He therefore concludes that there is no adsorption in the true sense. In a subsequent research,[94] he has examined the question of the taking up of heavy metals by cellulose and concludes that the action is due to the replacement of the bivalent anion of the ash by a hydrion or ion of a heavy metal, the action being analogous to the replacement of metals in the permutites. He surmises that ash-free cellulose would not take up metals at all, and shows in an earlier communication[95] that lead is not completely adsorbed from its solutions by cellulose of low ash alkalinity. He has also investigated the factors bearing on the adsorption of copper from solutions of copper salts, finding that the addition of ammonia causes a rapid increase in the amount of copper taken up. The question of the part played by the alkalinity of the ash in cellulose in the taking up of acids[96] has also received his attention, and he finds that, when the ash is almost completely removed, adsorption falls to zero. In the light of these results it is obvious that the ash content of cellulose

[91] *Biochem. Zeits.*, 1921, **115**, 134.
[92] *Le Papier*, 1921, **24**, 108.
[93] *Pharm. Weekblad*, 1921, **58**, 46; *J.*, 1921, 130A.
[94] *Ibid.*, 1921, **58**, 233; *J.*, 1921, 281A.
[95] *Ibid.*, 1921, **58**, 152.
[96] *Ibid.*, 1920, **57**, 1571.

must be taken into account when considering many of the phenomena associated with adsorption.

The question of the influence of various factors on the size of the cellulose aggregate is one of vital interest to all concerned in the production of solutions of cellulose and its derivatives. As pointed out in last year's report, pioneer work of a valuable nature has been carried out by W. H. Gibson and his collaborators,[97] who ingeniously applied methods of viscosity determination to an investigation of cellulose and the nitric esters prepared therefrom, and by J. Masson and R. McCall,[98] who have investigated the conditions affecting the preparation of nitrocellulose solutions for viscosity determination. These researches, which along with others, were carried out during the late war, had for their ultimate object the evolution of methods of control which would ensure the economical production of propellant explosives of uniform character, and as the outcome of this work large-scale experiments were conducted by the Directorate of Propellant Supplies in conjunction with the Research Department of the Royal Arsenal, Woolwich. The results of these experiments, which have been admirably correlated and summarised by R. A. Punter,[99] form a valuable source of information concerning the functions of the various treatments of cotton waste for nitrocotton manufacture. It is shown that, using wastes composed of cottons having widely different colloidal properties, it is possible, by the employment of a sufficiently drastic soda boil, to obtain a normal resistant cellulose of uniform size of aggregate, from which a nitrocotton of corresponding colloidal properties can be prepared, this resulting in ultimate conservation of solvent in the preparation of the finished cordite. The work affords an instance of the application of organised research to large-scale production.

An apparatus for the production of dispersoids by mechanical degradation has been devised by H. Plauson, and is described by C. Naske.[100] The possibilities of this "colloid mill" are dealt with by the inventor,[101] who claims that it will provide an improved process of preparing cellulose solutions. In conjunction with S. A. Vielle,[102] he patents a method for the production of colloidal suspensions of cellulose by mechanically disintegrating the substance in media of low electrical conductivity. P. P. von Weimarn[103] considers that the dispersive action, like the swelling of cellulose by aqueous salt solutions, is dependent on the activity of the

[97] *Chem. Soc. Trans.*, 1920, **117**, 473, 479; *J.*, 1920, 541A; *J.*, 1921, 172T.

[98] *Chem. Soc. Trans.*, 1920, **117**, 819; *J.*, 1920, 641A.

[99] *J.*, 1920, 333T.

[100] *Z. Ver. deuts. Ing.*, 1921, **65**, 495.

[101] *Z. angew. Chem.*, 1921, **34**, 469, 473; *J.* 1921, 799A.

[102] E.P. 155,836.

[103] *Kolloid Zeits.*, 1921, **29**, 198.

water of hydration associated with the salt. The solubility of cellulose in solutions of alkali and alkaline-earth salts has been examined by R. O. Herzog and F. Beck,[104] who also find it to be a function of the hydration of the ions of the respective salts, which they arrange in the following order of activity:—$NH_4 < K < Na < Li$; $Ba < Sr < Ca$; $\frac{1}{2}SO_4 < Cl < Br < I < CNS$. They have examined a large number of salts under different conditions, and define the various requirements to be fulfilled by salt solutions for swelling and solvent action.

One of the most important researches carried out during the year on the subject of cellulose solubility, is that of H. E. Williams,[105] who, in examining the solvent action of the metallic thiocyanates on cellulose, finds that the process is governed entirely by the physical condition of the salt, which must be a liquid hydrate—an associated molecular complex of salt and water, having a suitable boiling point, a viscosity above a defined minimum, and a positive heat of dilution between certain fixed limits. He deals with a large number of experiments on the action of the various thiocyanates on cellulose. Mercerising and parchmentising effects may be obtained by the treatment of cellulosic material with thiocyanate solutions under suitable conditions, and the process is likely to be of considerable industrial interest. The theoretical considerations on which he explains many of the results obtained will be published shortly. A patent which may be of interest to those concerned with the production of cellulose solutions is that of Z. Ostenberg,[106] who dissolves the material in a mixture containing calcium chloride and sulphuric acid of more than 60% strength.

The subject of the inflammability of cellulosic materials is of interest from the point of view of textiles and papers. An important research on the conditions governing the smouldering of cellulose has been carried out by H. v. Euler and K. O. Josephson,[107] who find that cellulose, which will not smoulder in air, may be made to do so by addition of suitable amounts of salts, preferably lithium and potassium compounds. The problem has been examined from ionic considerations. It is found that chlorine inhibits smouldering and that polyvalent ions, which are incapable of causing smouldering, may increase inflammability.

Constitution.

A considerable amount of important work has been carried out during the year on the constitution of cellulose, and of the carbohydrates associated with this substance in nature or produced

[104] *Z. physiol. Chem.*, 1920, **111**, 287; *J.*, 1921, 254A.

[105] *J.*, 1921, 221T.

[106] U.S.P. 1,355,415; *J.*, 1921, 114A.

[107] *Brennstoff-Chem.*, 1920, **1**, 63.

from it as the result of degradation processes. Various modes of attack have been directed towards arriving at a definite view of the configuration of the cellulose molecule employing chemical methods of investigation, but the results obtained are in many cases so conflicting as to leave the impression that the problem of the constitution of cellulose will continue to occupy the attention of chemists for many years to come. It is to be regretted that, with the exception of one or two investigations of fundamental importance, little appears to have been done on the subject from the physical and physico-chemical points of view.

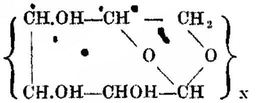
Scherrer, in an early paper,[108] found that cellulose appeared to consist of a heterogeneous arrangement of molecules when examined by the X-ray method for crystal structure. In more recent work R. O. Herzog and W. Janeke,[109] who have examined cellulose along with other organic substances of high molecular complexity by the X-ray spectrographic method of Debye and Scherrer,[110] state that the results obtained in the case of celluloses from cotton, ramie, and wood, evidence the existence of a rhombic system with an axial ratio 0·6935 : 1 : 0·4467. The examination was carried out with rods of compressed cellulose powders exposed to radiations from a specially constructed Coolidge tube with a copper anticathode. The cellulose powders employed were all of low ash content (cotton 0·03, ramie 0·03, and wood 0·1% ash, respectively).[111]

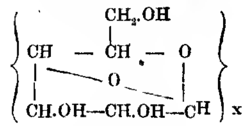
K. Hess and E. Messmer,[112] in examining the optical activity of cuprammonium solutions of cellulose, confirm the work of Levallois. Cellulose is found to have a high specific rotation $[\alpha] = -950°$ to $1000°$, while regenerated cellulose in solution in concentrated hydrochloric acid, and various cellulose derivatives in ethereal, aqueous-alkaline, and neutral salt solutions are inactive. Cellulose is stated to possess latent asymmetry, similar to that of the lower carbohydrates such as mannitol, which only becomes optically active in aqueous solution when borax is added. It is assumed that the action of the cuprammonium solution is analogous to that of borax.

In the course of a comprehensive summary of available information bearing on the constitution of cellulose, H. Hibbert,[113] after discussing the relative merits and demerits of the formulæ proposed by Tollens, Cross and Bevan, Vignon, Green, and Barthelmy, deals with the formula advanced by himself, which is similar to that of Vignon, in that both represent intramolecular condensation of the

[108] *Ges. Wiss. Gottingen Nachr.*, Sept., 1918, 96; *Sci. Abs.*, 1921, **24**, 229.
[109] *Ber.*, 1920, **53**, 2162; *cf. J.*, 1921, 342A.
[110] *Phys. Zeit.*, 1916, **17**, 277.
[111] *Z. Physik*, 1920, **3**, 196.
[112] *Z. physik. Chem.*, 1921, **98**, 14; *Ber.*, 1921, **54**, 834; *J.*, 1921, 342A.
[113] *J. Ind. Eng. Chem.*, 1921, **13**, 256.

aldehyde group of dextrose with two of its hydroxyls, but which is of doubtful value in the light of more recent work on the subject :—


Vignon.


Hibbert.

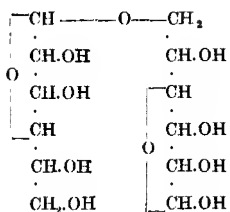
In a continuation of the article [114] he reviews the most important reactions of cellulose and the formation of cellulose derivatives and degradation compounds, from the point of view of his formula, suggesting a new type of synthesis for a substance which he considers closely allied to the cellulose nucleus as represented by this formula.

He criticises the work of K. Hess and W. Wittelsbach,[115] with whom he fails to agree on several points. The Hess-Wittelsbach formula, which represents cellulose (in ground structure) as a penta-dextrose glucoside of glucose, is selected on the assumption that a constant ratio exists between the amounts of octa-acetyl cellobiose and penta-acetyldextrose formed when cellulose is acetylated under certain conditions. Hibbert contends that the results obtained by Ost in earlier work and the variations in the values secured by Hess and Wittelsbach do not support the view of a constant ratio between cellobiose octa-acetate and dextrose penta-acetate formation. K. Hess and E. Messmer,[116] in the course of further work in support of the above formula, which, based on the Fischer formula for tannins, assumes the existence of an ether-like complex, have succeeded in synthesising similar complexes by condensing sugars with some of the higher fatty acids.

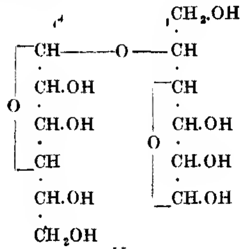
Cellulose being a particularly non-reactive substance, forming ill-defined derivatives, one naturally turns to its simpler degradation products for evidence which will throw light on its constitution. In this respect, cellobiose, bearing as it does much the same relationship to cellulose as maltose does to starch, in that it is formed as the result of the bacterial and enzymic degradations of cellulose,[117] presents an excellent starting point, and is now receiving the careful attention of chemists ; much excellent work is being carried out on the subject. W. N. Haworth and E. L. Hirst,[118] following up the earlier work of Haworth and Leitch,[119] in which the following

[114] *J. Ind. Eng. Chem.*, 1921, **13**, 334.
[115] *Z. Elektrochem.*, 1920, **26**, 232 ; *J.*, 1920, 512A.
[116] *Ber.*, 1921, **54**, 499.
[117] Pringsheim, *Z. physiol. Chem.*, 1912, **78**, 266.
[118] *Chem. Soc. Trans.*, 1921, **119**, 193 ; *J.*, 1921, 234A.
[119] *Ibid.*, 1919, **115**, 809.

formula for maltose (I) was established and a provisional formula (II) for cellobiose suggested, have now obtained experimental proof in support of the latter formula :—



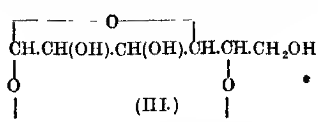
I.
Maltose.



II.
Cellobiose.

They have devised an improved method for the preparation of cellobiose in the form of its monopotassium derivative by acetolysis of cellulose followed by hydrolysis with alcoholic potash, and have methylated the product in two stages, obtaining a new derivative, heptamethyl methylcellobioside. By hydrolysis of this substance with dilute hydrochloric acid they obtain tri- and tetramethylglucoses of the butylene oxide type, the former being identical with the trimethylglucoses previously isolated from methylated lactose[120] and methylated cellulose.[121] From a consideration of the results of Hudson,[122] who examined the optical properties of lactose and cellobiose, it is probable that these two hexoses are structurally and stereochemically similar. Cellobiose is therefore considered to be a glucose-β-glucoside.

The grouping of hexoses in the cellulose molecule is still a matter for discussion. According to Haworth and Hirst there is evidence of a structural linking for the part of the glucose constituent of the type (III) which is linked with other residues through both the



(III.)

reducing group and the hydroxyl group attached to the fifth carbon atom from the reducing end of the hexose chain; this view is contrary to the opinion of Sarasin,[123] who regards cellulose as a polymeride of lævoglucosan.

[120] *Ibid.*, 1918, **113**, 188.
[121] *Ibid.*, 1914, **105**, 2364.
[122] *J. Amer. Chem. Soc.*, 1916, **38**, 1566.
[123] *Arch. Sci. phys. nat.*, 1918 [iv.], **46**, 5.

The problem of the constitution of cellobiose is also interesting investigators abroad. P. Karrer and F. Widmer[124] have studied the conditions governing the acetolysis of cellulose (whereby cellobiose is obtained as the octa-acetate) with the idea of deriving precise information concerning the maximum proportion of cellobiose obtainable from cellulose. They find that the low yields of octa-acetylcellobiose obtained on acetolysis of cellulose at a high temperature (105° C.) is due to the fact that 70% of the substance is decomposed, after formation, by the acetylysing mixture. They suppose that cellobiose complexes probably exist in cellulose to the extent of 50%, which is incompatible with the Hess-Wittelsbach formula, requiring as it does only 33% of pre-formed cellobiose. Later[125] they point out that the first step in determining the constitution of cellulose is to attack that of cellobiose, which they commence to do by examination of its methyl derivatives, obtaining heptamethyl-β-methylcelloside (heptamethyl methylcellobioside). The methods employed in the preparation of this substance are similar to those adopted by Haworth and Hirst, but in its subsequent hydrolysis[126] the authors make use of the formation of anilides in the separation of tri- and tetramethyl-glucoses. Like Haworth and Hirst, they conclude that cellobiose is a glucose-β-glucoside (5-β-α-glucosido-α-glucose). In view of these facts interesting results are quoted by M. Bergmann and H. Schotte,[127] who, by oxidising cellobial with perbenzoic acid, obtain as the final product 5-glucosido-mannose. In a subsequent article M. Bergmann[128] puts forward a new formula for cellobial based on these observations.

K. Freudenberg[129] finds that octa-acetylcellobiose is decomposed by acetolysis at ordinary temperatures, with formation of acetylglucose to the extent of 30% of the original substance. He concludes that, making allowances for the fact that this probably occurs during the acetolysis of cellulose, it may be reasonably supposed that cellobiose residues form 60% of the cellulose complex, even though the highest yields of the octa-acetylcellobiose obtained during cellulose acetolysis are much below this figure [Madsen, 43%[130]].

In the course of work on the acetolysis of carbohydrates, P. Karrer and C. Naegeli[131] converted diamylose and starch into acetobromomaltose by treatment with acetyl bromide under suitable conditions. M. Bergmann and F. Beck,[132] using a mixture

[124] *Helv. Chim. Acta*, 1921, 4, 174; *J.*, 1921, 342A.
[125] *Helv. Chim. Acta*, 1921, 4, 179.
[126] *Helv. Chim. Acta*, 1921, 4, 295; *J.*, 1921, 402A.
[127] *Ber.*, 1921, 54, 1564; *J.*, 1921, 596A.
[128] *Naturwiss.*, 1921, 9, 308; *Chem. Zentr.*, 1921, III., 214.
[129] *Ber.*, 1921, 54, 767; *J.*, 1921, 342A.
[130] Dissert., Hannover, 1917.
[131] *Helv. Chim. Acta*, 1921, 4, 169, 263; *J.*, 1921, 361A.
[132] *Ber.*, 1921, 54, 1574; *J.*, 1921, 596A.

of acetyl bromide, hydrobromic acid, and acetic acid similar to that employed by Karrer and Naegeli in some of their investigations, have obtained complete conversion of starch and maltose into acetobromoglucose, but only a 40% conversion in the case of cellulose; they are at present investigating the latter reaction. P. Karrer and F. Widmer,[133] in a later paper, give results of experiments in the treatment of cellulose with acetyl bromide in presence of glacial acetic acid, in which they obtain a partial conversion into acetobromocellose and acetobromoglucose, the greatest yield of acetobromocellose being 20%. They are unable to obtain any information as to whether cellulose is a condensed anhydro-sugar or chain compound.

In a review of work previously carried out on the hydrolysis of cellulose, J. C. Irvine and C. W. Soutar[134] point out that the yields of dextrose hitherto claimed by various observers have not been based on the actual amount of the sugar or of a definite derivative isolated, and are therefore unreliable. To determine if cellulose is essentially a polyglucose anhydride yielding a theoretical amount of glucose on hydrolysis, they have subjected cotton cellulose to acetolysis, hydrolysed the polysaccharide acetates formed, and by methylation of the products of hydrolysis, have obtained a total yield of pure crystalline methylglucoside amounting to 85% of the quantity theoretically possible if cellulose is composed entirely of dextrose residues. The complete elimination of the dextrose residues from the polysaccharide was accomplished with varying degrees of difficulty, and this fact is instanced as evidence of the non-uniformity of the dextrose linkages. It is presumed that the cellobiose constituent is the part of the cellulose molecule most resistant to hydrolysis.

A. Wohl and K. Blumrich,[135] in studying the action of dilute hydrochloric on cellulose, obtain indication that two substances are produced—glucose and a higher carbohydrate—the latter being capable of further hydrolysis. In a continuation of the work A. Wohl and A. Krull[136] have hydrolysed cellulose in two stages by first treating with fuming hydrochloric acid, followed by boiling with dilute acid, and as a result of this treatment obtain a yield of a reducing sugar corresponding to 97% of the theoretical amount. A result very similar to that noted by Wohl and Blumrich is obtained by Y. Kauko,[137] who, by employing moist hydrochloric acid gas as his hydrolysing agent, obtains along with glucose an unknown carbohydrate, which on further treatment in an autoclave is trans-

[133] *Helv. Chim. Acta*, 1921, **4**, 700; *J.*, 1921, 764A.

[134] *Chem. Soc. Trans.*, 1920, **117**, 1489; *J.*, 1921, 76A.

[135] *Z. angew. Chem.*, 1921, **34**, 17; *J.*, 1921, 158A.

[136] *Cellulosechemie*, 1921, **2**, 1; *J.*, 1921, 158A.

[137] *Naturwiss.*, 1921, **9**, 237; *J.*, 1921, 764A.

formed into glucose. He assumes that the cellulose forms an additive compound with hydrochloric acid during the first stage of the hydrolysis and hopes to obtain eventually a quantitative hydrolysis of cellulose by increasing the amount of hydrochloric acid employed.

In examining results previously obtained by Ost and Wilkening,[138] G. W. Monier-Williams,[139] employing their method of hydrolysis with 72% sulphuric acid, has succeeded by careful treatment of the products of hydrolysis, in isolating a yield of crystalline glucose corresponding to nearly 91% of the amount theoretically obtainable. This result is interesting in view of the observation made by Irvine and Soutar, and in that such a high yield of crystalline glucose has never been previously obtained by the hydrolysis of cellulose.

K. Hess, W. Wittelsbach, and E. Messmer[140] have extended acetolytic methods of examination to the ethyl ethers of cellulose, isolating and examining the products of the reaction. They find that in the first stages of the breakdown, gradual depolymerisation of the molecule takes place, and put forward some interesting theories of probable changes analogous, they suppose, to those occurring when cellulose is treated with cuprammonium solution.

The production of methyl derivatives of cellulose and starch by Denham and Woodhouse[141] opened up a new field in cellulose chemistry, and the subsequent researches by various investigators on these compounds and their hydrolytic cleavage products has done much to broaden our conception of the probable structure of the cellulose complex. In continuation of earlier work, W. S. Denham[142] has now succeeded (by repeated methylation of alkali cellulose, using dimethyl sulphate) in producing methyl ethers of high methoxyl content (up to 44·6% OCH_3), closely approximating to that of the theoretical trimethylcellulose (45·6% OCH_3), with a minimum degradation of the cellulose as evidenced by the low copper reduction figure and retention of fibrous structure. He finds that introduction of the methyl group into cellulose does not confer solubility in volatile solvents, and that with increase in methoxyl content, the solubility of the material in cuprammonium solution decreases. Products containing 40% OCH_3 are completely insoluble.

In connexion with the preparation of the higher alkyl ethers of cellulose, it is interesting to note that L. Lilienfeld[143] has patented

[138] *Chem.-Zeit.*, 1910, **34**, 461.

[139] *Chem. Soc. Trans.*, 1921, **119**, 803; *J.*, 1921, 539A.

[140] *Z. angew. Chem.*, 1921, **34**, 499; *J.*, 1921, 688A.

[141] *Chem. Soc. Trans.*, 1913, **103**, 1735; 1914, **105**, 2357; 1917, **111**, 244; *J.*, 1913, 974; 1914, 1084.

[142] *Ibid.*, 1921, **119**, 77; *J.*, 1921, 211A.

[143] E.P. 149,320; *J.*, 1922, 53A.

a method for the production of the more highly alkylated methyl, ethyl, benzyl, etc. ethers of carbohydrates (including cellulose, starch, dextrin, lichenin, and inulin) by further alkylation of the lower alkyl compounds in absence of, or in presence of only small amounts of water, regulating the amount of alkali employed.

It will be remembered that Pictet and his co-workers[144] have provided new methods for the degradational examination of carbohydrates by distillation *in vacuo*. J. Reilly,[145] employing Pictet's method, has subjected methylcelluloses to vacuum distillation. A series of these substances, prepared by the method of Denham and Woodhouse, and containing respectively 25·31, 28·1, 33·4, and 43·7% methoxyl (the first three products corresponding approximately with di-, and the fourth with tri-methylcellulose) were examined. The compound containing 28·1% of methoxyl gave on distillation 50% of a product apparently containing a dimethyl-lævoglucosan, which, when hydrolysed, yielded dimethylglucose. Reilly regards this fact as supporting Pictet's views that the cellulose molecule contains a lævoglucosan group.

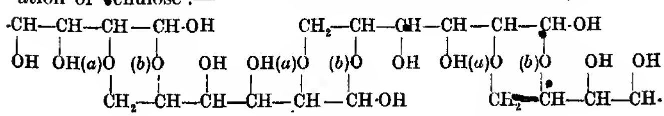
The subject of lævoglucosan is still receiving attention. J. Reilly[146] has obtained this substance by the vacuum distillation of sucrose. A. Pictet and J. Reilly[147] have prepared lævulosan and have examined certain of its properties, obtaining a trinitrate, a triacetate, and a tribenzoate, facts which point to the existence of three hydroxyls of alcoholic character in the molecule. Questions bearing on the structure of the anhydro-sugars closely allied to lævoglucosan and on the properties of these compounds have been investigated by A. and J. Pictet,[148] P. Karrer, F. Widmer, and A. P. Smirnov,[149] and P. Karrer.[150] A new method for the preparation of lævoglucosan, which, prior to its isolation by Pictet in the distillate from carbohydrates, had only been obtained by hydrolysis of certain glucosides, has been devised by P. Karrer and A. P. Smirnov,[151] who by treatment of acetobromoglucose with an alcoholic solution of trimethylamine, followed by saponification of the acetyl groups with an alkali or alkaline-earth solution, obtain a quantitative yield of this substance.

J. C. Irvine and J. W. H. Oldham[152] examine the relationship of lævoglucosan to glucose and to cellulose. In a critical review of Pictet's work, they point out that owing to the complexity of

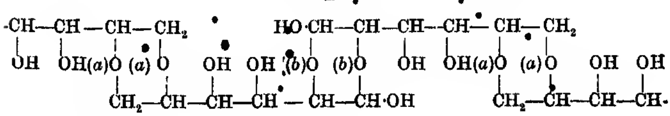
[144] *Helv. Chim. Acta*, 1918, **1**, 187 *et seq.*
[145] *Ibid.*, 1921, **4**, 616; *J.*, 1921, 540A.
[146] *J.*, 1921, 249T.
[147] *Helv. Chim. Acta*, 1921, **4**, 613; *J.*, 1921, 555A.
[148] *Ibid.*, 1921, **4**, 788.
[149] *Ibid.*, 1921, **4**, 796.
[150] *Ibid.*, 1921, **4**, 811; *J.*, 1921, 785A.
[151] *Ibid.*, 1921, **4**, 817; *J.*, 1921, 785A.
[152] *Chem. Soc. Trans.*, 1921, **119**, 1744; *J.*, 1922, 27A.

changes occurring during the decomposition of carbohydrates by heat, it is not reasonable to suppose that the degradation products obtained bear definite structural relationships to the original substances examined and that the views of Pictet, who supposes that cellulose and starch are polymerides of lævoglucosan, and who proposes radical changes in the accepted formulæ for certain natural glucosides, are not justifiable. Assuming that, as Pictet suggests, cellulose is a polymerised lævoglucosan, trimethylcellulose must be regarded as a polymeride of trimethyllævoglucosan, in which case the trimethylglucoses obtained by hydrolysis of trimethylcellulose and trimethyllævoglucosan will be identical. The authors have prepared and examined these substances and find that the trimethylglucose from trimethylcellulose is totally different from that obtained from methylated lævoglucosan prepared by Pictet's distillation method. As the result of these and other investigations, they are of the opinion that there is no structural relationship between cellulose and lævoglucosan. They show that lævoglucosan is 1 6-β-glucose anhydride, and suggest the expression "β-glucosan" for the older name. They agree with Pictet's[153] formula for the substance with certain reservations, pointing out that his explanation of the isomerism displayed by the so-called *d*- and *l*-glucosans, in which he regards both anhydrides as derived from the same form of glucose, is most im probable. They suppose the *d*-compound to be an anhydride of α-glucose just as the *l*-compound is now shown to be the 1.6-anhydride of β-glucose.

One of the most recent papers dealing with the general aspect of cellulose constitution is that of A. C. von Euler,[154] who, in the course of a discussion on the salient facts bearing on the subject, puts forward new formulæ for both cellulose and cellobiose. Two modifications of the cellulose formula, which, though containing the *p*-dioxan ring of Green's formula, admits of a chain of hexose molecules of any desired length, are proposed. It may not, however, satisfactorily explain some of the points connected with the methylation of cellulose :—



I.

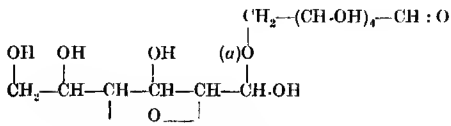


II.

[153] *Helv. Chim. Acta*, 1920, **3**, 649.
[154] *Chem.-Zeit.*, 1921, **45**, 977 ; *J.*, 1921, 764A.

Two types of oxygen linkings are represented in the formula, (*a*) being of the ether type, and (*b*) a semi-acetal combination, which, on addition of the elements of water (and subsequent fission in the latter case), would split to give : CH·OH + ·CH_2.OH and :CH·OH + ·CH:O, respectively.

Cellobiose is represented as



which, it will be noted, is similar to the formula proposed by Haworth and his co-workers,[155] with the exception of the type of oxygen linking and the arrangement of the carbonyl groups.

Cellulose Degradation Products.

The facts relating to the formation and properties of cellulose mucilage have been extensively examined by J. E. Minor.[156] It has been suggested that hydrocellulose is a cellulose aggregate containing adsorbed products of decomposition. Mucilage is stated to differ from hydrocellulose in that it contains a larger proportion of soluble adsorbed dextrins, and in its formation the presence of these substances is assumed to catalyse the hydrolytic decomposition of the parent cellulose. It has a highly-colloidal character and its probable formation during the dyeing of cellulose materials may explain some of the effects obtained.

The assumption that hydrocellulose is an aggregate of cellulose and cellodextrins is refuted by H. Ost and R. Bretschneider,[157] who, as the result of experimental evidence, consider it to be a normal decomposition product of cellulose; this view is supported by H. Pringsheim,[158] who, from consideration of the most recent work on cellulose structure, suggests that the hydrolytic rupture of the anhydroglucose ring would give rise to reactive products such as hydro- and oxy-cellulose. C. G. Schwalbe and E. Becker[159] have examined the properties of three varieties of hydrocellulose and find this substance to be less acid than oxycellulose and to be more easily attacked by alkalis. They have also investigated the resistance to alkalis, copper numbers, furfural yields and acidities of four varieties of oxycellulose, correlating the results, and note that whilst the amounts of furfural produced are practically

155 *Chem. Soc. Trans.*, 1919, **115**, 813; 1921, **119**, 193.
156 *J. Ind. Eng. Chem.*, 1921, **13**, 131; *J.*, 1921, 175A.
157 *Z. angew. Chem.*, 1921, **34**, 422; *J.*, 1921, 654A.
158 *Cellulosechemie*, 1921, **2**, 57.
159 *Zellstoff u. Papier*, 1921, **1**, 135; *J.*, 1921, 807A.

constant throughout the series, marked variations are observed in the case of the other three factors. It is claimed that oxycelluloses of both acidic and aldehydic characters have been identified. They have made further investigations on the action of barium hydroxide on oxycellulose, E. Becker having shown in a previous communication[160] that oxycellulose-barium compounds can be formed, and employed for the recognition of the substance. A new test for oxycellulose[161] is suggested, based on the fact that when suspended in water it reacts either alone or in presence of sodium chloride, with methyl orange, producing a coloration which varies from orange to dark red. This reaction, which is not shown by normal cellulose or by hydrocellulose, has been employed as a quantitative method of estimation.

A. J. Hall[162] describes a modification of the well-known silver reduction test for oxycellulose, which is claimed to give good results for the detection of this substance in cotton fabric. In examining the action of diazotised aromatic amines on various substances, A. E. Everest and A. J. Hall[163] state that oxidised cellulose is capable of reacting with diazotised amines of the benzidine type to form azo-compounds, a reaction not shown by normal cellulose.

E. Knecht[164] has examined the dyeing properties of an oxycellulose obtained by oxidation of cellulose with potassium permanganate and sulphuric acid, noting that when dyed from an alkaline bath it destroys direct cotton dyestuffs, without taking up any colour. It is dyed, however, by non-reducible dyes of the Primuline type, and on prolonged boiling in these solutions is removed. The dyeing properties of this particular oxycellulose may be restored on treating with stronger solutions of alkali. In a subsequent paper with F. P. Thompson[165] he states that cotton tendered by sulphuric acid shows the dyeing reactions of oxycellulose, the effect being due to the fixation of sulphur in some form by the cotton. It may be distinguished from oxycellulose in that its fibrous structure is destroyed, its affinity for basic dyes is increased, and on boiling with sodium hydroxide solution its affinity for direct cotton dyestuffs is not restored.

The action of hydrogen peroxide on cellulose has been investigated by R. Haller,[166] who finds that most vegetable fibres are degraded on prolonged immersion in 30% solutions of this substance.

[160] *Zellstoff u. Papier*, 1921, **1**, 3; *J.*, 1921, 653A.
[161] *Ber.*, 1921, **54**, 545; *J.*, 1921, 295A.
[162] *Textile Colorist*, 1921, **43**, 400.
[163] *J. Soc. Dyers and Col.*, 1921, **37**, 227.
[164] *Ibid.*, 1921, **37**, 76; *J.*, 1921, 255A.
[165] *Ibid.*, 1921, **37**, 270; *J.*, 1921, 841A.
[166] *Text.-Forschung*, 1920, **2**, 79.

He establishes the formation of a cellulose peroxide as an intermediate product in the reaction, which may be accelerated by the presence of chromium and certain dyestuffs. Alumina acts as a retarding agent, and its use in protecting fabrics against the destructive action of laundering agents containing peroxides is suggested.

V. Lenher[167] finds that selenium oxychloride does not attack cellulose or hydrocellulose substances.

Schulze's "hemicellulose" theory is discussed by E. Salkowski,[168] who, in the course of a criticism, emphasises the need for a clear definition of the term. In an article on the examination of celluloses, F. Lenze, B. Pleus, and J. Mueller[169] advocate determination of oxy- and hemicelluloses in special circumstances. Hemicelluloses are estimated by hydrolysis, followed by separation of the mannose as the *p*-bromophenylhydrazone, and the oxycelluloses obtained by difference after removal of the hemicelluloses. The occurrence of hemicellulose-splitting enzymes and the processes involved in the animal digestion of hemicelluloses are dealt with by A Rippel.[170]

A. Krogh and H. O. Schmidt-Jensen[171] have investigated the fermentation of cellulose in the paunch of the ox; their technique is criticised by W. Klein.[172]

J. Groenewege[173] in investigating the bacterial degradation of cellulose, attributes decomposition to the enzyme cellulase. The bacterial decomposition of hemicelluloses has been examined by T. Shimizu.[174]

Cellulose Ethers, Esters, etc.

The preparation of cellulose ethers is one of the most interesting developments in cellulose chemistry during recent years.

Reference has already been made to the more recent work on the chemistry of these substances, to a discussion on their possible employment in artificial silk manufacture, and to the patent of L. Lilienfeld.[175]

H. Dreyfus has protected methods for the production of cellulose ethers suitable for the manufacture of celluloid-like masses, kinematograph films, varnishes, and the like,[176] by suitable treatment of specially-prepared alkali cellulose with dialkyl sulphates or alkyl

[167] *J. Amer. Chem. Soc.*, 1921, **43**, 33.
[168] *Z. physiol. Chem.*, 1921, **114**, 31; *J.*, 1921, 465A.
[169] *J. prakt. Chem.*, 1920, **101**, 213.
[170] *Landw. Versuchs-Stat.*, 1921, **97**, 179; *J.*, 1921, 824A.
[171] *Biochem. J.*, 1920, **14**, 686.
[172] *Biochem. Zeits.*, 1921, **117**, 67.
[173] *Med. Geneesk. Lab. Weltevreden*, 1920, 163; *J.*, 1921, 76A.
[174] *Biochem. Zeits.*, 1921, **117**, 227.
[175] E.P. 149,320; *J.*, 1922, 53A.
[176] E.P. 164,374, 164,375, 164,377; *J.*, 1921, 540A.

halides, and suggests the use of alkylated aromatic sulphonamides[177] as solvents for these bodies. He also describes the preparation of a new class of cellulose derivatives obtained by the action of halogenated glycols, polyhydric alcohols or their ethers on alkali-cellulose, whereby the residue introduced into the cellulose molecule contains one or more hydroxyl groups.[178]

Cellulose ethers appear to form suitable bases for the production of plastic masses having high insulating power, great stability, and possessing water-resisting properties. G. Leysieffer[179] proposes to employ them for the manufacture of electrical insulators, and the Bayer Co.[180] claim that when incorporated with the oily or resin-like condensation compounds obtained by the action of halogenated alkylbenzenes on aromatic hydrocarbons, the resulting products are suitable for the preparation of insulating materials, varnishes, and for use as waterproofing agents.

R. O. Herzog, A. Hildesheimer, and F. Medicus[181] deal with the production of nitrocellulose films and varnishes with special reference to the use of solvents and softening agents and their effect on the physical character of the final product. In an interesting and fairly comprehensive article, L. Clement and C. Riviere[182] discuss cellulose-ester varnish technology, with regard to the production of varnishes for many specific purposes, and give methods for the analytical examination of these products

W. L. Barnett[183] obtains clear and colourless acetylcelluloses, with minimum decomposition of the parent complex, by acetylating with mixtures of acetic acid and acetic anhydride, using as a mixed catalyst, chlorine and sulphur dioxide. By varying the ratio of chlorine to sulphur dioxide, and controlling the temperature, the degree of acetylation may be regulated. Details of a method for the analytical hydrolysis of cellulose acetates are given.

The Verein f. Chem. Ind. in Mainz[184] describe methods for the acetylation or esterification of cellulose, or feebly nitrated cellulose, under conditions which allow of only a minimum of liquefaction of the product of the reaction during the treatment.

Methods for the production of chloroform-insoluble cellulose acetate are protected (as an addition to an earlier patent[185]) by the Soc. Chim. des Usines du Rhône and others.[186]

177 E.P. 164,384, 164,385, 164,386; *J.*, 1921, 540A.
178 E.P. 166,767; *J.*, 1921, 654A.
179 E.P. 156,762; *J.*, 1921, 732A.
180 G.P. 336,476; *J.*, 1921, 577A.
181 *Z. angew. Chem.*, 1921, **24**, 57; *J.*, 1921, 220A.
182 *Chim. et Ind.*, 1921, **6**, 283.
183 *J.*, 1921, 8T.
184 G.P. 335,359; *J.*, 1921, 505A.
185 E.P. 13,696 of 1914; F.P. 473,399; *J.*, 1915, 488.
186 E.P. 146,092; *J.*, 1921, 765A.

Interesting investigations of the action of hydrazines on cellulose acetate have been made by W. L. Barnett.[187] By heating di- and tri-acetylcelluloses with phenylhydrazine or *p*-bromophenylhydrazine, in suitable solvents, he obtains compounds of the ketosehydrazone type, of definite melting point. From a study of the nitrogen and bromine contents of these substances he assumes that a progressive degradation of the cellulose complex takes place, and that by rupture at the oxygen linkages, compounds containing active ketonic groups are produced.

The British Cellulose Co., J. F. Briggs, and C. W. Palmer[188] find that treatment of acetate silks, in various forms, with solutions of thiocyanates (ammonium thiocyanate is specially mentioned) results in increase of the absorptive power of these materials for dyestuffs. In a later patent, the British Cellulose Co. and J. F. Briggs[189] claim to increase the affinity for dyes of articles made from the lower acetates of cellulose, by subjecting them to a superficial hydrolysis with alkalis. This may be effected during dyeing, by addition of caustic soda to the dyebath (using dyes which are not affected by this reagent), or may be carried out prior to dyeing. It is stated that any desired shade of colour may be obtained by varying the degree of hydrolysis. Crêpe effects are stated to be obtained on filaments and threads of acetate silk by treating them with solutions of ammonium thiocyanate or acetic acid under suitable conditions.[190]

There are few developments to record in connexion with the production, utilisation, and properties of the nitrocelluloses.

Graphical methods for the simplification of calculations involved in the preparation of nitrating acid mixtures for the manufacture of nitrocotton are described by R. A. Fowler.[191]

The employment of viscosity measurements as an indication of the stability of nitrocelluloses is proposed by J. Duclaux,[192] who finds that a relation exists between reduction in viscosity and loss of weight occurring when nitrocellulose is heated.

G. Carlsson and E. Thall[193] propose to reduce the viscosity of nitrocellulose solutions by heating them in an autoclave, the required viscosity being obtained by regulation of the temperature and time of heating.

An interesting paper on the action of light on nitrocellulose is contributed by B. Homolka,[194] who states that nitrous acid, liberated

[187] *J.*, 1921, 61T.
[188] E.P. 158,340; *J.*, 1921, 213A.
[189] E.P. 169,741; *J.*, 1921, 808A.
[190] E.P. 165,164.
[191] *J.*, 1921, 166T.
[192] *Bull. Soc. Chim.*, 1921, 29, 374; *J.*, 1921, 530A.
[193] E.P. 136,141; *J.*, 1921, 296A.
[194] *Phot. Korr.*, 1920, 57, 239; *J.*, 1921, 27A.

as the result of its photochemical decomposition, can be detected with 9-aminophenanthrene (with which it reacts to give 9.9′-azoxyphenanthrene) and makes use of this fact to obtain a red photographic image on a specially-prepared collodion paper containing this indicator.

Theories of nitrocellulose constitution are discussed and advanced by G. de Bruin,[195] who also gives details, with graphs, of experimental results bearing on ether-alcohol solubility, stability and nitrogen content, obtained during an examination of nitrocelluloses prepared on a technical scale. There is stated to be no relation between ether-alcohol solubility and nitrogen content; on the other hand, stability is found to decrease with increasing nitrogen content. The author makes reservations concerning the interpretation of these results.

Numerous patents have appeared dealing with the preparation of alkali-cellulose and the production of viscose therefrom, but the majority present no very novel features. A process for the rapid manufacture of a matured alkali-cellulose is outlined by A. Thilmany,[196] who proposes to digest cellulose with alkali *in vacuo* at a high temperature. C. L. Stulemeyer[197] also claims a vacuum impregnation treatment in preparing alkali cellulose, and states that the action may be accelerated by increasing the gas pressure to 3–4 atmospheres after the initial vacuum digestion.[198]

W. L. Barnett[199] has investigated the action of chloro-acyl chlorides on cellulose and examined the properties of the products obtained.

The Akt.-Ges. f. Anilinfabr.[200] propose to acetylate nitrocelluloses of low nitrogen content obtained by the combined action of nitric acid and nitrobenzene on cellulose, employing for the purpose acetic acid-acetic anhydride acetylating mixtures with bromine or other suitable substances as catalyst. By treating mercerised cellulose with chloracetic acid or its homologues in presence of alkali, the Deutsche Celluloid Fabrik of Eilenberg[201] claim to obtain water-soluble salts of cellulose-acetic (or other) acid, which are suitable for use as glue and gelatin substitutes.

As in late years the patent literature contains many claims for the production of plastics from cellulose esters, and a variety of new solvents for these substances are proposed. Amongst the more novel may be mentioned methylene chloride, cyclohexane, its homologues

[195] *Rec. Trav. Chim.*, 1921, **40**, 632; *J.*, 1921, 903A.
[196] G.P. 328,035; *J.*, 1921, 175A.
[197] E.P. 167,199; *J.*, 1921, 689A. Niederl. Pat., Cl. 29b, 13,798, 1919.
[198] E.P. 167,201; *J.*, 1921, 689A.
[199] *J.*, 1921, 253T.
[200] E.P. 145,524; *J.*, 1921, 577A.
[201] G.P. 332,203; *J.*, 1921, 344A.

and isomers, aromatic sulphonamides, and a variety of mixed solvents. Naphthenic acid and acetin (free from monoacetin and acetic acid) figure in certain plastic compositions.

WOOD, STRAW, ETC.

An enormous amount of information bearing on the science and technology of wood, and on the utilisation of this and allied vegetable products as a source of cellulose, has appeared during the year.

The structure of pine wood has been exhaustively examined by A. Abrams,[202] who, employing microchemical methods, has determined the relative resistance of the various tissues to a number of reagents.

The properties of lignified tissue have been the subject of further investigations. In investigating the absorptive power of plant tissues L. Rosenthaler[203] finds that lignified membranes take up both ferric and ferrous salts, the former to the greater extent, whereas those composed of cellulose do not absorb these substances. P. Casparis[204] has compared the absorptive power of lignified and non-lignified cell walls for certain acids, bases, and salts, and suggests the use of solutions of cobalt thiocyanate as a test for lignified matter, with which it gives a blue colouration. Vanadic acid is stated by J. Grüss[205] to react with lignin, producing a yellowish brown colour, which is destroyed by ammonia, but may be intensified on treatment with chromic acid. The addition of phosphoric acid to the vanadic acid is said to aid the reaction.

E. C. Crocker[206] suggests that the colour reactions developed on treating lignified tissue with phloroglucinol and *p*-nitraniline are due to the presence of aldehydes invariably associated with this material. It is stated that Maule's test may be used to distinguish between deciduous and coniferous woods. The former develop a bright red, and the latter a faint brown coloration when subjected to the reaction.

The constituents of sulphite waste lye, with special reference to the mode of occurrence of *a*-lignin, have been examined by K. H. A. Melander,[207] who, from analyses of the free, so-called "*a*-lignin sulphonic acid," concludes that the existence of a well-defined sulphonic acid cannot be assumed. In a later communication[208] he gives details of the preparation of a number of compounds of this substance with aromatic amino compounds, and concludes that its acidic character is due to the sulphur-containing

[202] *J. Ind. Eng. Chem.*, 1921, **13**, 786; *J.*, 1921, 731A.
[203] *Ber. Deuts. Pharm. Ges.*, 1921, **31**, 27.
[204] *Pharm. Monats.*, 1920, **1**, 121, 137, 153; *cf. J.*, 1921, 343A.
[205] *Ber. bot. Ges.*, 1921, **38**, 361.
[206] *J. Ind. Eng. Chem.*, 1921, **13**, 625; *J.*, 1921, 654A.
[207] *Cellulosechem.*, 1921, **2**, 41; *J.*, 1921, 465A.
[208] *Ibid.*, 69; *J.*, 1921, 621A.

group. He is also of the opinion that α-lignin is a mixture of substances derived by degradation of a parent substance originally present in wood.

Methods for the isolation of lignin from winter-rye straw have been examined by E. Beckmann, O. Liesche, and F. Lehmann,[209] who, from consideration of results of molecular weight determinations, methoxyl estimations, and examination of various benzoyl derivatives, ascribe to it the formula $C_{40}H_{44}O_{15}$, in which the existence of four methoxyl and four hydroxyl groups is assumed. The molecular weight is found to be 764·6, and the equivalent weight, 382·3.[210] This latter result is subsequently discussed, in the light of his own results by F. Paschke,[211] who finds that lignin obtained from straw by treatment with sodium carbonate, differs in oxygen content from that obtained by the Beckmann-Liesche process.

The mechanism of the sulphite treatment of wood has been examined by P. Klason,[212] who states that the reactions involving the removal of lignin by the sulphite are influenced by the hydrogen-ion concentration of the liquor. Methods for the estimation of lignin are discussed by H. Krull,[213] who employs digestion with hydrochloric acid gas for the purpose.

No new methods for the determination of cellulose appear to have been devised. The relative merits of several well-known processes of cellulose estimation are considered and criticised by B. Johnsen, S. A. Mahood, and W. H. Dore.[214] F. Herig[215] gives a description of a convenient form of apparatus for the carrying out of the Cross and Bevan chlorination treatment. Problems bearing on the removal of pentosans from wood cellulose,[216] and on the nature of the residual material after its treatment with alkali,[217] are dealt with by E. Heuser and E. Boedeker, and by C. G. Schwalbe and E. Becker.

U. Pomilio[218] gives details concerning the use of chlorine in the small and large scale preparation of pure cellulose. Solutions of chlorine peroxide in aqueous and volatile solvents are employed by E. Schmidt[219] as agents for the separation of pure cellulose from wood.

[209] *Z. angew. Chem.*, 1921, **34**, 285; *J.*, 1921, 539A.
[210] *Biochem. Zeits.*, 1921, **121**, 293; *cf. J.*, 1921, 732A.
[211] *Z. angew. Chem.*, 1921, **34**, 465; *J.*, 1921, 732A.
[212] *Svensk Kem. Tidskr.*, 1921, **33**, 141.
[213] *Papierfabr.*, 1921, **19**, [22A], 65.
[214] *J. Ind. Eng. Chem.*, 1921, **13**, 358.
[215] *Cellulosechem.*, 1921, **2**, 34.
[216] *Z. angew. Chem.*, 1921, **34**, 461; *J.*, 1921, 688A.
[217] *Zellstoff und Papier*, 1921, **1**, 93; *J.*, 1921, 731A.
[218] *Chim. et Ind.*, 1921, **6**, 267.
[219] G.P. 331,907; *J.*, 1921, 295A; *cf. J.*, 1921, 764A.

P. Waentig and W. Gierisch[220] describe the chlorination, and subsequent treatment of wood shavings for cellulose and fibrous-material production.

New reagents for the preparation of cellulose from wood have been employed by R. Hartmuth,[221] who proposes to use a treatment with phenols and phenolic substances, W. Schlosser,[222] who protects a process involving condensation of the non-cellulose impurities with primary and secondary aliphatic and aromatic amines, and R. Schwarzkopf,[223] who subjects the raw material to the action of inorganic and organic acid chlorides. Details of an extensive series of analytical examinations of wood cellulose are given by F. Lenze, B. Pleus, and J. Mueller.[224]

Numerous investigations of woody and other sources of cellulose have been made. B. Rassow and A. Zschenderlein,[225] in a paper on the composition of hemp wood, discuss their own analytical results in comparison with those previously obtained by C. G. Schwalbe and E. Becker.[226] They suggest, from several considerations, that pentosans are intermediate products in the natural synthesis of lignin.

P. Klason[227] revises earlier figures obtained during an analytical examination of spruce wood, stating that he now finds the composition to be: cellulose (free from pentosans), 53%; hemicellulose, 15%; lignin, 30%; other substances, 2%. The composition of reeds (*Phragmites communis*) has been investigated by F. Herig,[228] with special reference to the presence of silicic acid in their tissues, and its removal during the various processes in the manufacture of paper from these plants.[229]

M. Ishikawa[230] describes the examination of "Ashi" fibre, obtained from a Japanese reed. It resembles straw in microscopical and chemical characters, and in its reactions. Results of analyses are given.

An almost pure specimen of xylan has been obtained from straw cellulose by E. Heuser,[231] who has also studied its hydrolysis, obtaining a 60% yield of xylose. Examinations of the content of soluble carbohydrates present in pinewood felled at different

[220] *Textil-Forsch.*, 1920, **2**. 69.
[221] G.P. 3??,705; *J.*, 1921, 144A.
[222] G.P. 328,729; *J.*, 1921, 144A.
[223] G.P. 328,730; *J.*, 1921, 144A.
[224] *J. prakt. Chem.*, 1921, **101**, 213.
[225] *Z. angew. Chem.*, 1921, **34**, 204; *J.*, 1921, 576A.
[226] *Ibid.*, 1919, **32**, 126; *J.*, 1919, 408A.
[227] *Svensk Pappers-Tidning*, 1921, **24**, 7.
[228] *Cellulosechem.*, 1921, **2**, 25 44; *J.*, 1921, 382A, 465A.
[229] *Ibid.*, 1921, **2**, 44; *J.*, 1921, 465A.
[230] *J. Chem. Ind. Tokyo*, 1920, **23**, 1153; *J.*, 1921, 113A.
[231] *Papierfabr.*, 1921, **19**, [22A], 79.

times of the year have been made by S. Schmidt-Nielsen,[232] who has obtained evidence of the presence of 28% of xylose in an extract prepared from winter-felled pinewood. W. H. Peterson, E. B. Fred, and J. H. Verhulst[233] find that crude xylose syrup is readily fermented under suitable conditions of hydrogen-ion concentration and calcium carbonate content of the medium, by *B. acetoethylicum*, with production of acetone, ethyl alcohol, formic and acetic acids.

Laboratory experiments on the production of methyl alcohol from lignin obtained as a by-product of wood extraction have been made by E. Heuser and H. Schmelz,[234] who find that the greatest yield of methyl alcohol (about 15%) is obtained by digesting the material with dilute hydrochloric acid under a pressure of from 5 to 6 atmospheres, for two hours.

In the course of an investigation of humus formation, V. A. Beckley[235] has made experiments to determine if the decomposition of cellulose by an organism, *Spirochæta cytophaga*, which he found in rotting straw, results in production of hydroxymethylfurfural, and has obtained negative results. Studies of the digestive action of the fungus, *Xylaria Hypoxylon*, on isolated constituents of cell walls, show that of a number of substances examined, pectin and xylose are the most readily attacked, whereas starch and xylan are comparatively resistant. The experiments were made by C. L. Gatin and M. Molliard,[236] who find that lignin is also decomposed by the organism.

The constituents of cork and cutinised tissues have been the subject of an interesting series of investigations by J. H. Priestley and his co-workers.[237] In the course of the investigations, experiments have been made on the waterproofing action of salts of phellonic acid.

Wood Pulp.

Various articles have appeared in the technical journals dealing with extensions of the pulp industry, and with the establishment of new technical schools and institutes for the prosecution of pulp and paper research.

Several new materials have been examined from the point of view of pulp production, but little of any special interest has appeared. Details of examinations of, and methods for the manufacture of pulp from papyrus, are given by R. Four-

[232] *Tekn. Ukeblad*, 1920, **67**, 354; *J.*, 1921, 342A.
[233] *J. Ind. Eng. Chem.*, 1921, **13**, 757.
[234] *Cellulosechem.*, 1920, **1**, 6; *J.*, 1921, 41A.
[235] *J. Agric. Sci.*, 1921, **11**, 69; *J.*, 1921, 232A.
[236] *Rev. Gén. Bot.*, 1920, **32**, 216.
[237] *New Phytologist*, 1921, **20**, 17.

nier.[238] S. D. Wells[239] has made boiling trials of oat hulls and examined their suitability for conversion into straw boards and paper. C. Groud[240] reviews the possible utilisation of the barks of plants of the mallow and mulberry families. The sulphate treatment of bamboo, and the qualities of the products obtained therefrom are dealt with by J. Stevens.[241]

The mechanism of the various processes proposed for the pulping of lignified matter are discussed by C. G. Schwalbe,[242] who from economic considerations holds that the hydrolysing agents used in the present sulphite and sulphate treatments are the only satisfactory ones at present available. Analytical methods for the control of the sulphite process are proposed by R. Sieber. He recommends methods for the determination of free and total acids,[243] and lime[244] in sulphite liquors. He suggests measurement of the digestion of the pulp by determination of the chlorine absorbed by samples from a standard solution of bleaching powder.[245] A. Chambovet[246] has pointed out that as organic acids are produced during the boiling process, acidimetric titration of the sulphite liquor during cooking does not give a true measure of the free SO_2. He outlines a scheme of analysis involving the physico-chemical separation of these substances.

Rapid methods for the control analysis of sulphate liquors are proposed by G. K. Bergman,[247] who employs a suitably-arranged series of alkali and sulphide determinations. B. N. Segerfelt[248] gives a description of the Rinman modification of the sulphate process, which involves cooking with a weak solution of caustic soda, in presence of a reducing agent (preferably mercury) at a temperature not exceeding 170° C.

Numerous accounts of investigations of the efficiency of the processes in pulping have appeared in the various journals, and special attention has been devoted to examination of the steam consumption in the boiling and drying processes. In these connexions attention may be directed to the papers of H. Brahmer,[249]

[238] *La Papeterie*, 1921, **43**, 386.

[239] *Pulp and Paper Mag.*, 1921, **19**, 1139 ; *J.*, 1921, 883A.

[240] *Le Papier*, 1921, **24**, 4.

[241] *Paper Industry*, 1921, **3**, 84.

[242] *Zellstoff und Papier*, 1921, **1**, 11 ; *J.*, 1921, 653A.

[243] *Svensk Pappers-Tidning*, 1920, **23**, 418 ; *Paper*, 1921, April 6, 24 ; *J.*, 1921, 382A.

[244] *Zellstoffchem. Abhandlungen*, 1920, **1**, 1.

[245] *Zellstoffchem. Abhandlungen*, 1920, **1**, 53 ; *Paper*, 1921, April 6, 17 ; *J.*, 1921, 382A.

[246] *La Papeterie*, 1920, **42**, 866, 914, 966.

[247] *Pulp and Paper Mag.*, 1921, **19**, 11.

[248] *Pulp and Paper Mag.*, 1921, **19**, 452 ; *Paper Ind.*, 1921, **3**. 96.

[249] *Svensk Pappers-Tidning*, 1920, **23**, 269.

H. Alfthan,[250] and to a communication from the Swedish Paper-Pulp Office, in which economy in heat utilisation is discussed.[251]

The decay of pulp wood, its effect on the consumption of the reagents employed in pulp manufacture, and on the yields of pulp produced, has been exhaustively examined by E. Sutermeister.[252] J. S. Bates[253] gives details of sulphite boiling tests carried out on average wood, infected wood, and chipper dust, as the result of which it is stated that infected wood may be used for sulphite pulp production if decay is limited to discoloration, and that chipper dust pulp might be satisfactorily blended with ordinary sulphite pulp, and so utilised.

C. Kress[254] has studied the action of the various moulds and fungi commonly found on pulp-wood and pulp, and has examined papers made from infected material. Investigations on the preservation of pulp wood and pulp have been undertaken by the American Paper and Pulp Association in conjunction with the U.S. Forest Products Laboratory. Of the substances so far examined only borax, sodium fluoride, and sodium dinitrophenolate proved to be commercially applicable.[255]

Comparative estimations of lignin in samples of unbleached, shredded Mitscherlich sulphite-cellulose have been made by E. Heuser and G. Wenzel,[256] who discuss the relative merits and demerits of the methods employed. The grading of wood celluloses on the basis of lignin content is suggested by H. Krull,[257] who, in the course of interesting analytical results obtained during an examination of typical pulps, gives the following figures for the lignin content of Mitscherlich and Ritter-Kellner pulps :—

	Mitscherlich.	Ritter-Kellner.
Hard ..	6·5—7·0% ..	7·5—9·5
Normal	5·5—6·0 ..	6·5—7·5
Soft (easy bleaching)	5·0—5·5 ..	4·5—6·5
Bleached	1·0—2·0 ..	——

He proposes to judge the chemical condition of pulps by their "corrected" copper values.

A dye test for distinguishing between unbleached sulphite and sulphate (Kraft) pulps is described by R. E. Lofton and M. F. Merritt,[258] who make use of the differential staining effects obtained

[250] *Papierfabr.*, 1919, **19**, 657 ; *J.*, 1921, 883A.
[251] *Svensk Pappers-Tidning*, 1921, **24**, 30.
[252] *Pulp and Paper Mag.*, 1921, **19**, 687 ; *J.*, 1921, 540A.
[253] *Ibid.*, 1921, **19**, 733 ; *J.*, 1921, 576A.
[254] *Ibid.*, 1920, **18**, 1225 ; *J.*, 1921, 75A.
[255] *Paper*, 1921, July 20, 20 ; *J.*, 1921, 577A.
[256] *Papierfabr.*, 1921, **19**, 1177 ; *J.*, 1921, 807A.
[257] *Ibid.*, 1921, **19**, [22A], 65 ; *J.*, 1921, 883A.
[258] *Techn. Assoc. Pulp and Paper Ind.*, 1920, **3**, 1 ; *J.*, 1921, 343A.

on treatment with a freshly prepared mixture of aqueous solutions of Malachite Green and Fuchsine.

M. G. Kotibhasker[259] has evolved a new method for determining the amount of mechanical wood in mixed pulps and papers. The process consists essentially in treating the material to be examined with a weak acid solution of *p*-nitraniline until absorption of this reagent by the mechanical wood is complete; the excess of *p*-nitraniline is then obtained by adding a known excess of titanous chloride solution, and titrating back with standard iron alum solution. The method is stated to be only applicable when the amount of mechanical wood in the sample exceeds 20%. For determination of amounts below this figure he recommends the well-known colorimetric method of C. F. Cross.

K. G. Wilen[260] describes a method for testing the strength of Kraft pulps. The process involves screening and beating the pulp under standard conditions, and the preparation of sheets, which are tested on a Mullen machine. Recommendations concerning the expression of results are made.

Waste Liquor.

The utilisation of waste liquor still continues to form the subject of numerous articles and patents, and, while many of the suggestions present considerable ingenuity, it is doubtful if they will find commercial application.

Its possible use as a binding agent for roads and briquetted fuels, and its employment in the preparation of tanning agents, and as a means for the cheap production of alcohol, have been exhaustively reviewed, and methods for its application in several of these and other connexions patented. The use of sulphite liquor as a motor fuel can be made practicable by the employment of suitable vaporising devices.[261] A description of a new apparatus for obtaining carbon and other products from sulphite liquors is given by A. Klein.[262] O. Aschan[263] discusses the utilisation of cymene obtained as a by-product of the sulphite process, and states that a yield of cymene of 90–95% purity, suitable for the indirect preparation of azo dyes, T.N.T., thymol, and carvacrol, may be recovered to the extent of 1 kg. per ton of pulp produced.

Methods for the titration of sulphite waste liquors have been reviewed by R. Sieber,[264] who has also made experiments on the aldehyde content of fermented sulphite liquor in conjunction with

[259] *J. Soc. Dyers and Col.*, 1921, **37**, 11; *J.*, 1921, 113A.
[260] *Paper*, 1921, Dec. 20, 15, 36; *J.*, 1921, 175A.
[261] *Papir-Journalen*, 1920, **8**, 109.
[262] *Papier-Zeit.*, 1921, **40**, 634.
[263] *Zellstoffchem. Abhandlungen*, 1920, **1**, 73.
[264] *Zellstoffchem Abhandlungen*, 1920, **1**, 95.

determination of the amounts of alcohol present.[265] B. Holmberg[266] has examined sulphite liquor lactone, obtained by the ether extraction of sulphite waste liquors, and gives details of its physical and chemical characters. It is stated to be converted by the action of sulphuric acid into a monosulphonic acid, which on treatment with water, yields a hydroxy-acid. In a later communication, in conjunction with M. Sjöberg,[267] he gives details of the preparation of its methyl derivatives, with reference to the reactions of the latter substance.

Alkali lignins have been obtained by B Holmberg and T. Wintzell,[268] who have separated them from the precipitates obtained by acidification of the black liquor from the soda-cellulose process. They have obtained a- and λ-lignin, have studied their chemical properties and prepared their methyl derivatives. E. Wahlberg[269] has previously attempted to separate the constituents of alkali waste liquors by subjecting them to dialysis.

Numerous methods for the utilisation and deodorisation of gases evolved during the various cooking processes have been protected. The subject would appear to present many openings for fruitful investigation. The disposal of untreated waste liquors in pulp-producing districts is also a matter for careful consideration, and is of as vital importance as the disposal of trade effluents in some of our large textile industrial centres.

The recommendations of a Commission appointed to deal with strawboard factory effluents in Holland are dealt with by A. Hermann,[270] who gives details of a plant operating to utilise the gaseous products of the anaërobic fermentation of these liquors for power-gas production.

Paper.

Extensions of the pulp and paper industries, and the investigation of new sources of raw material to determine their possible employment for pulp production, have already been dealt with.

For some time past numerous attempts have been made by the French paper-makers and technologists to exploit their natural resources, and investigations of the paper-making qualities of various indigenous plants have been undertaken from time to time.

The suitability of the stem of the sunflower as a source of paper pulp has been exhaustively examined by the Paris Chamber of

[265] *Svensk Pappers-Tidning,* 1920, **23**, 336.

[266] *Svensk. Kem. Tidskr.*, 1920, **32**, 56; *J.*, 1921, 113A. *Ber.*, 1921, **54**, 2389; *J.*, 1921, 884A.

[267] *Ber.*, 1921, **54**, 2406; *J.*, 1921, 884A.

[268] *Ber.*, 1921, **54**, 2417; *J.*, 1921, 884A.

[269] *Zellstoffchem. Abhandlungen*, 1920, **1**, 92.

[270] *Het Gas*, 1920, **40**, 131; *J.*, 1921, 343A.

Commerce, whose results are reviewed by R. Fournier.[271] He also gives a list of a number of plants found in France or her colonies which might possibly be utilised in the paper industry,[272] the same subject having been dealt with by C. Groud,[273] who, in the course of a later article[274] discusses the possible utilisation of vine shoots in papermaking. He states that France (exclusive of Algeria) produces a sufficient quantity of vine shoots to furnish 720,000 tons of pulp annually. Details of an extensive series of laboratory tests by "Cellulose et Papiers," on the pulping and papering of a variety of raw materials, have been given.[275]

Examinations of "falasco," a heterogeneous collection of cryptogamous and aquatic plants obtained from the Pisan marshes, have been made by G. L. Pavarino and G. Castellari,[276] who have carefully studied the microscopical, physical, and chemical characters of the fibres of the vegetable constituents of this material, which they consider to be suitable for paper manufacture. "Falasco" is also discussed by C. Groud,[277] from the standpoint of the yields of pulp obtained from the various plants present in the mixture.

"Taboca Brava" and "Aninga," of Brazilian origin are stated to be suitable for the manufacture of wrapping papers of various qualities.[278]

Other vegetable materials suggested or used for papermaking are peat,[279] "sugamo"[280] (a Japanese seaweed), and "okra,"[281] which is being exploited in America.

In connexion with the detection of mechanical wood in mixed pulps, reference may be made to the cobalt thiocyanate test for lignified tissue proposed by P. Casparis,[282] which may be of value for this purpose.

The process of rag-boiling, and the effect of the various factors in the treatment of fibrous materials for paper manufacture have been reviewed from the points of view of efficiency and character of the half-stuff produced, by H. Grimm.[283] It is stated that the mechanical treatment to which material is subjected in the washing and in the half-stuff hollander, modifies the chemical constituents

[271] *La Papeterie*, 1921, **43**, 242.
[272] *Le Papier*, 1921, **24**, 116.
[273] *Le Papier*, 1920, **23**, 217.
[274] *Le Papier*, 1921, **24**, 114.
[275] *Chim. et Ind.*, 1920, **4**, 529.
[276] *Staz. sper. agar. ital.*, 1920, **53**, 32.
[277] *Le Papier*, 1920, **23**, 259.
[278] *Bull. Imp. Inst.*, 1920, **18**, 323 ; *J.*, 1921, 383A
[279] E.P. 168,355 ; *J.*, 1921, 733A.
[280] E.P. 153,804 ; *J.*, 1921, 6A.
[281] *Paper*, 1921, **27**, 16.
[282] *Pharm. Monats.*, 1920, **1**, 121, 137, 153 ; *J.*, 1921, 343A.
[283] *Zellstoff und Papier*, 1921, **1**, 7, 33 ; *J.*, 1921, 653A.

of tho fibre very considerably. Questions affecting tho degree of hydration of sulphite and esparto pulps during the beating process have been discussed.[284] It is pointed out that sulphite pulps, may, under certain circumstances, have a marked tendency to rapid hydration, which is undesirable in the manufacture of papers for printing or writing. This may be corrected by admixture of esparto pulp, which, being a soda pulp, does not hydrate readily. The use of the Schopper-Riegler apparatus in making tests of the degree of beating of paper pulp is dealt with.[285]

H. Press[286] has investigated the dyeing of pulps in the hollander with reference to the production of coloured cardboard from straw pulps and gives details of the absorption of direct cotton, basic, and acid dyes by this material. J. Huebner[287] has also made an interesting series of experiments on the dyeing of paper pulp, and proposes to obtain fast shades by the precipitation of acid dyes by basic dyes within this substance, giving details of a useful combination of colouring matters for employment in this connexion.

The amount of published material dealing with the bleaching of paper pulps is small and is mainly composed of semi-popular articles, several of which deal with the application of electrolytic bleaching processes to the paper industry.

Interesting observations on the bleaching of soda and sulphate pulps prepared from coniferous woods have been made by S. D. Wells,[288] who has examined the action of bleaching-powder solutions on these materials. He finds that the alkali-solubility of the pulps increases with increase in the strength of bleaching liquor employed, and that considerable degradation of the cellulose takes place before the colour is removed, indicating the unsatisfactory nature of this type of bleach. He obtains slightly more satisfactory results as regards colour removal by carrying out the bleach treatment in two stages with an intermediate washing. The pentosan contents of the pulps were found to be unaffected by bleaching, but on the other hand their methoxyl contents were reduced by the treatment.

Problems connected with the sizing of paper and employment of various sizing materials have formed the subject of several interesting articles which have appeared in the various journals.

The observations of E. Arnould[289] on the inhibitive effect of small quantities of sodium chloride absorbed by the cellulose, on the sizing of paper by the rosin-alum process, have already been mentioned. Methods for the control of the alum content of the

[284] *La Papeterie*, 1921, **43**, 146.
[285] *Le Papier*, 1920, **23**, 255.
[286] *Papierfabr.*, 1921, **19**, 261, 365; *J.*, 1921, 383A.
[287] *J. Soc. Dyers and Col.*, 1921, **37**, 139; *J.*, 1921, 382A.
[288] *J. Ind. Eng. Chem.*, 1921, **13**, 936; *J.*, 1921, 807A.
[289] *Le Papier*, 1921, **24**, 108.

tubsizing bath are discussed by P. W. Codwise,[290] who recommends the use of bromothymol blue as an indicator in carrying out titrations.

F. Stöckigt and A. Klingner[291] deal with the use of colloidal resin as a sizing agent, giving details of its mode of preparation and the factors affecting its coagulation. The paper forms an interesting study in applied colloid chemistry. In an account of the new "Zellkoll-Amal"[292] process for the sizing of fine papers, in which use is made of formaldehyde-glue or alum-formate-glue gels, the satisfactory fixation of various loading materials is discussed, and it is claimed that the process is remarkably efficient in this respect.

A. Kolb[293] gives details concerning the employment of alkali soaps as substitutes for resin in paper sizing. R. Miller[294] deals with the practical aspect of the casein coating of papers. J. G. Vail[295] gives an account of the employment of sodium silicate as a sizing material. Numerous filling agents for papers have been discussed. E. G. Milham[296] reviews the various properties to be considered in the selection of paper fillers. Wilkinite[297] or jelly-rock, a highly colloidal clay, is proposed as a substitute for china-clay.

The patent literature connected with the sizing and filling of paper contains details of a large number of sizing and filling agents, among which are to be found carbohydrates, proteins, and their addition compounds, resinous substances, hydrogenated resins, and formaldehyde condensation products, along with a number of combinations of various substances for filling purposes.

In connexion with the production of papers for specific purposes, attention may be directed to the patent of C. G. Schwalbe,[298] who proposes to effect parchmentisation of stock in the edge runner, or in the hollander, by treatment with oxidising agents, obtaining in this way material which may be subsequently converted into parchment paper, and to that of the Zellstofffabr. Waldhof,[299] who claim that by treatment of sulphite pulp to be used for cigarette-paper manufacture, with alkalis, the unpleasant taste is removed.

The application of Batik printing to the production of novel effects on papers forms the subject of an article by L. Kollmann,[300]

[290] *Pulp and Paper Mag.*, 1921, **19**, 499; *J.*, 1921, 465A.
[291] *Papierfabr.*, 1921, **19**, [22A], 50; *J.*, 1921, 884A.
[292] *Paper*, 1921, **27**, No. 18, 13.
[293] *Papierfabr.*, 1921, **19**, 1141; *J.*, 1921, 807A.
[294] *La Papeterie*, 1921, **43**, 157.
[295] *Chem. and Met. Eng.*, 1921, **23**, 823; *J.*, 1921, 884A.
[296] *Paper Industry*, 1920, **2**, 1375, 1438.
[297] *Paper*, 1920, Dec. 8, 19, 34; *J.*, 1921, 175A.
[298] G.P. 303,305; *J.*, 1921, 144A.
[299] G.P. 327,735; *J.*, 1921, 144A.
[300] *Papierfabr.*, 1921, **19**, [22A], 39; *J.*, 1921, 884A.

in the course of which a description of the technique of the process is given.

Articles dealing with the utilisation of waste paper are few in number. B. Haas [301] deals with the removal of printing inks from this material. The recovery of stock from newsprint has received the attention of C. Baskerville and R. Stevenson.[302] The former author, in conjunction with C. M. Joyce,[303] gives details of the treatment of waste book paper.

The amount of published work dealing with the testing of papers is comparatively small. In the course of a report on the use of iodine solutions in paper examination, G. Wisbar [304] makes recommendations concerning the use of stannic chloride and iodine, calcium chloride and iodine, and aluminium chloride and iodine, along with the well-known zinc chloride-iodine reagent.

R. Fournier [305] describes an ingenious apparatus for measuring the translucency and opacity of papers which embodies the use of a selenium cell as a photometer. By employing a modified form of this apparatus the reflecting powers of papers may be determined.

The testing of the water-absorbing properties of paper for paper-yarn manufacture is discussed by F. Herig.[306]

In connexion with the climatic deterioration of papers, attention may be directed to the interesting communication by J. J. Sudborough and M. M. Mehta,[307] who from a study of the perishing of paper in Indian libraries, make certain recommendations concerning the preservation of, and the precautions to be observed in the preparation of papers for use in the Indian Plains stations.

[301] *Chem.-Zeit.*, 1921, **43**, 913 ; *J.*, 1921, 765A.

[302] *J. Ind. Eng. Chem.*, 1921, **13**, 213 ; *J.*, 1921, 295A.

[303] *Ibid.*, 1921, **13**, 214 ; *J.*, 1921, 295A.

[304] *Mitt. Materialprüf.*, 1920, **38**, 316 ; *J.*, 1921, 689A.

[305] *Le Papier*, 1920, **23**, 257 ; *Paper*, 1921, Feb. 9, **32**, 44 ; *J.*, 1921, 343A.

[306] *Papierfabr.*, 1921, **19**, [22A], 32 ; *J.*, 1921, 882A.

[307] *J. Indian Inst. Sci.*, 1920, **3**, 119 ; *J.*, 1921, 76A.

BLEACHING, DYEING, PRINTING, AND FINISHING.

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During the past year there have been many developments in pure science, more particularly in reference to the structure of atoms. The aim of physicists is to find such particulars of the structure of atoms as will enable them to explain their properties and forecast facts at present unknown. A great deal of the work published is mainly speculative. Bohr's theory explains the spectrum of hydrogen in a remarkable way, but so far has not explained that of helium. Langmuir's theory explains in an equally remarkable manner the properties of lithium hydride, sulphur fluoride, and many other compounds, but gets into difficulty with some quite simple substances such as carbon monoxide and cyanogen. Technologists are anxious to see further developments, more particularly in the domain of organic chemistry; a detailed knowledge of carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine is required for this purpose. So far as the building up of the carbon compounds is concerned the recent work on the structure of organic crystals by Bragg* is very promising, and we hope to see the work extended to the textile fibres. For this, workers are needed.

It would not be correct to say that similar developments have not taken place in the domain of textile technology; all one can say is that comparatively few chemists are engaged compared with the enormous number of problems awaiting to be solved.

The Department of Scientific and Industrial Research has extended its activities to the flax, silk, and laundering industries, and as would be expected from an impartial body of organisers, a similar system has been adopted as for industries other than those relating to textile processes.

The general idea appears to be the bringing together of several types of men, commercial, technical, and scientific. The impression has been given to many commercial men that one need only import science into an industry to effect something of a revolutionary character, the terms science and industry being used in a general

* *Proc. Phys. Soc.*, 1921, **36**, 33.

sense. Nothing has been said about the period during which the science has to get fused into the industry nor has much in the way of flux been used.

The solving of technical problems is not merely a question of mixing science and technology ; too often the result is an emulsion, of low degree of dispersion, and not a solution. An intimate knowledge of an industrial process and of those particular branches of science necessary for development must exist in the same train before much progress can be made. This condition cannot be secured without much experience—experience of the kind which can scarcely be explained since it is acquired by the exercise of those senses which are incapable of expression in concrete terms and accumulated in the form of ideas equally difficult of expression. Such experience is to be found in the practical men, many of whom have not the ability to express themselves accurately on quite simple matters.

Undoubtedly the works is the place for industrial research, since it is only there where one meets the necessary stimulus to produce something of commercial value. The sight of men working, the sound of machinery, and the obvious skill of the English work-people all have a great influence in producing an industrious research worker. The criticism which must be met from the more intelligent workpeople is the best preventive against the production of impracticable ideas.

Finally, the manipulation of a process in the treatment of tons of material gives one that intimate knowledge of mass-action which one cannot realise from a laboratory experiment.

Industry requires trained men possessing confidence in their own ability to tackle a problem throughout all its stages, and such confidence can only be acquired when the knowledge of the technical process and of the science underlying it exist in the same brain. The sooner this is realised by those responsible for the organisation of research the better for the success of the various research schemes. It is well to realise that the average practical man has just as much ability to acquire scientific knowledge as the average scientifically-trained man has to acquire technical skill.

Wool Scouring.

Several articles have been published relating to the extraction of grease by means of solvents. H. Hey[1] suggests that this is the method of the future for the treatment of wool when the prejudice which exists against it has been overcome. The writer has seen cases where dirty wool after extraction of the grease with solvents could not be obtained clean by subsequent washing with soap.

[1] *J. Soc. Dyers and Col.*, 1921, 37, 81, 183.

The suggestion was made that the removal of the grease to which the dirt adhered allowed that dirt to come in actual contact with the fibre substance. This suggestion appeared to be supported by the observation that clean wool was stained by an aqueous extract of the dirty solvent-extracted wool. It would appear advisable, therefore, to leave a little grease in the wool so as to leave the latter in a water-repellant state. The prejudice which exists to-day is undoubtedly the result of experiences such as that just mentioned, and will only be overcome by more satisfactory tests. Unfortunately, it is difficult to persuade those who have had unsatisfactory experiences to make further trials, in spite of the fact that one cannot arrive at perfection without meeting with many difficulties and overcoming them.

Hey states that the non-inflammable hydrocarbons such as carbon tetrachloride and di- and tetrachloro-ethylene tend to develop acid under the influence of heat and moisture. This is contrary to the generally accepted idea of the stability of these compounds and is well worth investigating. It is possible that the trouble may have been caused by a trace of dissolved chlorine.

J. I. Craven[2] describes the methods used in the United States. The gains for the solvent process are summarised thus :—(1) A gain in weight of clean fibre secured from a given amount of greasy wool as compared with soap scouring. (2) A reduction in noilage in combing, due to the avoidance of breaking or matting of fibre. (3) A great saving in soap and alkalis used for washing. (4) The use of wool-oil as lubricant in place of olive oil in subsequent processes of manufacture. (5) The by-products of the wool hitherto lost—wool fat and potash—can be sold. (6) Superior working qualities of the tops and yarn produced. Whether these claims can be substantiated for every class of wool is a question for the future and might conveniently form a subject for investigation by one or other of the numerous research associations.

A certain amount of work has been done on the scouring properties of mineral colloids, particularly those containing silica and alumina.[3] While these may find uses, the attraction which wool possesses towards most colloidal matters may cause difficulties since mineral matter does not improve the handle of wool.

It has been suggested[4] to use neutral or acid scouring solutions, the alkalinity of a soap being removed by the addition of lipolytic substances, Twitchell's reagent, etc. Whether these solutions would be efficient is an open question ; the writer never found an acid frothing agent which had any scouring properties.

[2] *Ibid.*, 1921, **37**, 235.

[3] G. Weissenberger, *Kolloid-Zeits.*, 1920, **27**, 69 ; *J.*, 1921, 18A.

[4] S. Aschkenasi, G.P. 329,008 ; *J.*, 1921, 211A.

As regards the theory of scouring L. L. Lloyd[5] attempted to remove insoluble soaps from pieces by the aid of soap and glue and claimed that according to the colloidal theory of scouring the glue should have enabled the soap to remove the insoluble soap. Few colloid-chemists would agree with this contention.

Some interesting points about the ordinary wool-scouring process are given by J. Schofield,[6] who has recently published a book on the subject.

References may also be made to papers on the action of water on wool,[7] the alkalinity of pure and commercial soaps,[8] the ultrastructure of soaps,[9] and determination of washing power of detergents.[10]

Scouring and Boiling Vegetable Fibres.

The solvent process has been applied to linen and cotton both for the improvement of the bleaching process[11] and in certain cases, to avoid bleeding and staining of dyed goods.[12] The question of cost is of more importance than in the case of wool since the alkaline boiling of cotton is, generally speaking, a cheap process.

The use of Ludigol (sodium *m*-nitrobenzenesulphonate) as an assistant in the boiling of fabrics containing coloured effects is discussed by J. M. Matthews.[13]

Bleaching.

An interesting note is given by A. F. McCulloch[14] relating to the behaviour of bleaching powder in the tropics and the advantage of a large excess of free lime is shown. The effect of alkalinity on the oxidising properties of hypochlorites is discussed by E. K. Rideal and A. R. Evans,[15] and the use of free hypochlorous acid prepared by the direct action of chlorine on water is protected by G. Ornstein.[16]

[5] *J. Soc. Dyers and Col.*, 1921, **37**, 101.

[6] *Ibid.*, 1921, **37**, 103.

[7] A. Reychler, *Bull. Soc. Chim. Belg.*, 1920, **29**, 291; *J.*, 1921, 174A.

[8] F. C. Beedle and T. R. Bolam, *J.*, 1921, 27T, 74T.

[9] W. F. Darke, J. W. McBain, and C. S. Salmon, *Proc. Roy. Soc.*, 1921, A **98**, 395; *J.*, 1921, 268A.

[10] P. Heermann, *Textilber.*, 1921, **2**, 37, 61; *J.*, 1921, 176A

[11] S. H. Higgins, E.P. 102,892; *J.*, 1917, 211.

[12] J. D. Lumsden, R. W. R. Mackenzie, E. H. Robinson, and M. Fort, E.P. 165,198; *J.*, 1921, 579A.

[13] *J. Soc. Dyers and Col.*, 1921, **37**, 236.

[14] *J.*, 1921, 240T.

[15] *J.*, 1921, 64R.

[16] E.P. 147,069; *J. Soc. Dyers and Col.*, 1921, **37**, 255.

The bleaching of cotton by means of perborates and persulphates forms the subject of an article by W. Kind.[17] For wool the use of hydrogen peroxide followed by treatment with hydrosulphite is patented by J. Kershaw.[18] The use of nitrosylsulphuric acid for the bleaching of silk in the gum or partially degummed state is discussed by E. Cagliostro.[19]

Of books published during the year that by S. H. Higgins on "Bleaching" is worthy of commendation. The information collected together is sufficiently wide to satisfy most readers.

Prolonged bleaching with chemick has been found to produce less tendering than when perborates in alkaline solution are used.[20] A method of analysing bleaching liquors by reaction with hydrogen peroxide is given by M. Schrero.[21]

Mercerising.

The originator of the present-day mercerising process, Mr. Horace Lowe, has recently been presented with the Perkin Medal by the Society of Dyers and Colourists.[22] In reviewing the history of the process, Mr. Sutcliffe Smith[23] mentioned that the lustre was noticed before the actual manner of producing it had been worked out. The treatment of cotton with caustic soda under tension and washing in that condition was first patented in 1890 and forms the process used to-day the whole world over. Mr. Sutcliffe Smith expressed the opinion that it was unfortunate that the term mercerising should have been used for Mr. Lowe's process and that a word should have been adopted which associated the process with his name.

It is unfortunate in many ways that the word "mercerising" should be used for products not produced by any method mentioned in Mercer's patent. Nowadays, the term would undoubtedly be used for any process of producing modified fibrous cellulose giving the characteristic blue colour with iodine and zinc chloride or strong potassium iodide; nevertheless, there are methods of treating cellulose to give this reaction which are not mentioned in Mercer's patent, such as, for instance, treatment with thiocyanates. There are also methods[24] of imparting a permanent lustre to either cotton or mercerised cotton which are not dealt with in Lowe's patent. In face of such developments it becomes more and more

[17] *Textilber*, 1921, 2, 325; *J.*, 1921, 691A.

[18] E.P. 162,198; *J.*, 1921, 385A.

[19] *Color Trade J.*, 1921, 13; *J. Soc. Dyers and Col.*, 1921, 37, 255.

[20] P. Heermann and H. Frederking, *Textilber.*, 1921, 2, 249, 277; *J.*, 1921, 578A; *cf.* *J.*, 1921, 542A.

[21] *J. Ind. Eng. Chem.*, 1921, 13, 559; *J.*, 1921, 578A.

[22] *J. Soc. Dyers and Col.*, 1921, 37, 135.

[23] *Ibid.*

[24] A. Hancock, *ibid.*, 1921, 37, 113.

necessary to use distinguishing terms. Comparative tests have been made [25] with solutions of sodium and potassium hydroxides which confirm the results obtained by E. Knecht and W. Harrison in 1912.[26] A. Liebmann [27] obtains special crêpe effects by local drying of fabrics before passing into a solution of caustic soda.

The mercerisation of fabrics containing viscose usually presents difficulties due to the damage or even destruction of the viscose. Processes for overcoming this trouble consist in the addition of formaldehyde, phenol, or potassium acetate to the caustic soda.[28] [29]

DYEING.

The paper on the dyeing of artificial silks published by L. P. Wilson and M. Imison [30] is one of outstanding importance. Most dyers are familiar with the irregularity in the dyeing property of artificial silk particularly in fine deniers. These authors have drawn up a list of dyestuffs which dye solid or nearly solid shades on viscose silk even when a considerable difference exists in the affinity of different parts of the silk for most direct cotton colours. They showed that dyestuffs of low molecular weight gave level dyeings whilst those of high molecular weight produced unlevel results. This offers considerable support to the electrical theory of dyeing, the relative size of fibre pores and dye particles being the important factor in this case. Any differences in the size of fibre pores would produce little difference in dyeing effect if the dye particles were very small, but if the latter were nearly as large as the fibre pores the dyeing effect would vary considerably.

There are other factors besides the molecular weight of the dyestuff to be taken into account, because one often meets pairs of dyestuffs which, from their constitutional formula, should behave in opposite relation to that which actually exists in their level-dyeing properties. Temperature is an important factor as also is the nature of the other ingredients present in the dyebath.

A considerable amount of work has been done in recent years on the dyeing of cellulose acetate, and a summary of the work has been published by J. F. Briggs.[31]

The methods proposed are detailed below :—

(1) Hydrolysis of the cellulose acetate with formation of hydrated cellulose, which absorbs dyestuffs in a similar manner to artificial silk composed of cellulose. Briggs mentioned that

[25] *Ibid.*, 1918, **28**, 224.

[26] E. Ristenpart, *Textilber.*, 1921, **2**, 130 ; *J.*, 1921, 255A.

[27] *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 484 ; *J.*, 1921, 255A.

[28] S. M. Jones, U.S.P. 1,343,138-9 ; *J.*, 1920, 542A.

[29] S. M. Jones and. O. Harlow, U.S.P. 1,392,833 ; *J.*, 1921, 809A.

[30] *J.*, 1920, 322T.

[31] *J. Soc. Dyers and Col.*, 1921, **37**, 287.

an old bath containing products of hydrolysis was more effective than a fresh one. This appears contrary to the ordinary laws governing hydrolysis since the products formed generally retard hydrolytic reactions. Briggs also showed that the hydrolysis is greatest at the surface and gradually decreases towards the centre. This opens out some very interesting theoretical points. The saponification and dyeing processes can, if desired, be carried out simultaneously.

(2) Swelling of the silk with ammonium thiocyanate [32] followed by dyeing with certain acid and basic colours. This process only improves the affinity of the silk for the dyestuffs and does not impart affinity where it did not previously exist. The improvement is undoubtedly due to the development of surface by the swelling process. The same treatment improves the dyeing properties of wool.[33]

(3) Dyeing with basic colours. This proceeds without mordanting, but the exhaustion of the dyebath is not very good. The addition of salts assists the dyeing in a similar manner to that met with in cotton dyeing. The fastness to light of the resulting dyeings is, in one or two cases, greater than that of the same dyestuff on tanned cotton.

(4) Dyeing with gallocyanine derivatives. This proceeds in a similar manner to the process with basic colours and in a few cases the absorption is very good.

(5) Dyeing with developed colours. Cellulose acetate has a strong affinity for organic bases and such can be diazotised and developed on the fibre in the usual way. Neither the diazotisation nor the development proceeds in the manner usually met with in dealing with such dyeings and occasionally one finds entirely different colours produced.

(6) Alizarin dyestuffs dye directly without a mordant in virtue of their phenolic and ketonic functions but the shades are not the same as those usually obtained with the alizarins when dyed on mordants, neither can such shades be secured by after-mordanting.

(7) Azo dyes. Certain sulphonated azo colours have an affinity for cellulose acetate and can be dyed direct from a bath containing salt.

(8) Vat dyes. Some of these can be applied from a bath containing ammonium salts to reduce the hydrolysing effect of the caustic soda usually employed. Ammonia does, however, hydrolyse the silk and must be used carefully if hydrolysis is to be avoided.

The introduction of a new product such as cellulose acetate necessarily brings forward new sets of problems for the dyer and

[32] J. F. Briggs, E. W. Palmer, and Brit. Cellulose Co., E.P. 158,340; *J.*, 1921, 213A.

[33] M. König, *Textilber.*, 1921, 2, 178; *J.*, 1921, 385A.

the production of solid shades in mixtures of this product with cotton, wool, or silk is perhaps the most difficult of these.

Nothing really new in dyeing processes for cotton, wool, and silk has been produced during the past year.

A process analogous to the production of Nitroso Blue is described by Wahl and Guindon,[34] a mixture of a nitroso compound and a diamine being used for the dyeing of wool.

A claim is made by F. Bayer und Co.[35] for improving the fastness to light of dyeings on wool by after-treatment with phosphotungstates, the process being applicable to dyestuffs containing sulpho- and amino-groups.

The use of fustic as a developer for diazotised amines in place of β-naphthol has been suggested by F. A. M. Noelting.[36]

A series of dyeings with tannic acid as developer is described by A. E. Everest and A. J. Hall[37] who mentioned a German Patent (55,837) as having covered part of this work.

A red dyestuff not hitherto used in dyeing is obtained by coupling *m*-nitro-*o*-anisidine with Naphthol A.S.[38]

A rapid method of producing dyeings of this type is mentioned by F. M. Rowe and E. Levin.[39]

The influence of the degree of dispersion of dyestuff in the indigo vat on the colour and fastness of the dyeings obtained is discussed by M. Freiberger.[40]

Theory of Dyeing.

An extremely interesting paper is that on the co-ordination theory of adjective dyeing by G. T. Morgan.[41] The effect of chelate groupings in the formation of metallic compounds of dyestuffs is described, such compounds seldom showing the ordinary chemical properties associated with the metal present. It is interesting to see the manner in which physics is gradually forcing itself on the notice of the chemist. Werner's theory of co-ordination, which discards the hypothesis of fixed or constant valency, was originally produced to explain the existence of complex inorganic substances. The more recent developments arising from the work of Thomson, Rutherford, and the Braggs and developed by Bohr, Lewis, Langmuir, and many others, will undoubtedly play a

[34] *Rev. Gén. Mat. Col.*, 1920, **24**, 179 ; *J.*, 1921, 77A.

[35] E.P. 143,242 ; *J.*, 1921, 385A.

[36] Soc. Ind. de Rouen, Note No. 1074 ; *J. Soc. Dyers and Col.*, 1921, **37**, 90.

[37] *J. Soc. Dyers and Col.*, 1921, **37**, 227 ; *J.*, 1921, 691A.

[38] W. Kielbasenski and C. Benedek, *Textilber.*, 1921, **2**, 281 ; *J.*, 1921, 579A.

[39] *J. Soc. Dyers and Col.*, 1921, **37**, 204 ; *J.*, 1921, 621A.

[40] *Textilber.*, 1921, **2**, 84 ; *J.*, 1921, 175A.

[41] *J. Soc. Dyers and Col.*, 1921, **37**, 43 ; *J.*, 1921, 175A.

very great part in the chemistry of the future. The new generation of chemists should miss no opportunity of becoming familiar with the electrical explanation of chemical phenomena. As far as dyeing theories are concerned we are rapidly approaching the time when we need not argue about the relative merits of solution-, surface-tension-, or adsorption theories, chemical or electrical theories: they all prove to be electrical phenomena. It is with full knowledge of the developments some of which are not yet published that the writer asserts that the electrical theory has come to stay, whether it be written in chemical or electrical language. The importance of intramolecular spacing in fibres cannot be overestimated; it enters into nearly every example of dyeing. Recent work by Haller[42] deals mainly with the application to wool of the electrical theory as developed by W. Harrison.[43]

PRINTING.

No important advances in printing have been published during the past year.

Useful notes on battick printing are given by L. Kollmann.[44]

Interesting observations on the effect of anthraquinone derivatives in assisting the discharge of *a*-Naphthylamine Claret are described by M. Battegay, A. Lipp, and H. Wagner.[45]

An explanation of the function of manganese dioxide in producing a reserve under indigo is given by R. Haller,[46] who recommends the use of a zinc-lime vat instead of a hydrosulphite vat for this purpose. There is no doubt that the effect is due to the formation of a semi-permeable membrane of manganese dioxide which coats itself with precipitated indigo by oxidation of the indigo-white at the surface of contact. The manganese dioxide must be formed on or in the thickening agent and not only on the fibre or a clear white will not be obtained. This is to be expected since the film is not strong enough to withstand any mechanical disturbance.

The production of ornamental effects by the action of pressure on moist fabrics prior to dyeing, as described by W. Warr,[47] is not new, having been used by the writer in 1906. The process was not sufficiently practical to warrant further work being done.

FINISHING.

The production of transparent effects on cotton by the action of sulphuric and nitric acids is the subject of a patent by J. E.

[42] R. Haller, *Kolloid-Zeits.*, 1921, **29**, 95; *J.*, 1921, 655A.

[43] *J. Soc. Dyers and Col.*, 1911, **27**, 279.

[44] *Chem.-Zentr.*, 1921, **92**, 35; *J.*, 1921, 145A.

[45] *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 233; *J.*, 1921, 655A.

[46] *Textilber.*, 1921, **2**, 173; *J.*, 1921 385A.

[47] The Calico Printers Assoc., Ltd., and W. Warr, E.P. 166,346; *J.*, 1921, 622A.

Pollak.[48] The process is similar to that described in numerous patents by Heberlein and is apparently applied with success on the Continent for the treatment of light muslins.

A claim is made for the production of wool-like effects on cotton fabrics by the use of casein, serum albumin, and other proteid substances treated with concentrated mineral acids either before or after application to the fabric. Starch is said to act in a similar manner.[49]

The supposed interlocking of the scales of wool as an explanation of felting still appears to hold its fascination[50] in spite of the fact that it has been proved untenable.

S. H. Higgins and A. Hodge[52] give an interesting article on the preparation of cloth for finishing. This article discusses the numerous faults in woven fabrics which prevent finishers from producing good results. The advantages to be gained by closer co-operation between manufacturers and finishers are put forward.

Sizing.

It has been proposed to use a mixture of china-clay and a neutral silicate as a sizing agent in place of starch, the size being removed by water prior to bleaching.[53] As silicates are readily decomposed by the carbon dioxide of the air, it would be interesting to learn how much of the product would be removed by water after six months' exposure to air. In later patents[54] colloids are added to the silicate, presumably to prevent the fixation of the silica by the action of carbon dioxide.

Proofing.

Where fabrics dyed with various types of dyestuff are required to be made waterproof, the vulcanising process described by S. J. Peachey[55] offers many advantages over the older processes. Peachey's process consists in the treatment of the rubbered material alternately with hydrogen sulphide and sulphur dioxide; the sulphur produced in this reaction at once vulcanises the rubber. Where thicker layers of rubber have to be vulcanised, such as in tyres, it is apparently advantageous to use one or both of the gases under pressure.

[48] E.P. 167,864; *J.*, 1921, 691A.

[49] Soc. Gillett et Fils, F.P. 506,188 and 506,403, *J. Text. Inst.*, 1921, **12**, 90.

[50] F. Hardcastle *J.*, *Soc. Dyers and Col.* 1921, **37**, 117.

[51] W. Harrison, *ibid.*

[52] *J. Textile Inst.*, 1921, **12**, 268,

[53] A. Poulson, E.P. 152,096; *J.*, 1920, 779A.

[54] A. Poulson, E.P. 163,103 and 163,915; *J.*, 1921, 506A, 766A.

[55] *J.*, 1921, 5T.

With reference to tyres, an interesting paper is given by R. Truesdale and C. Hayes,[56] showing the behaviour of rubbered fabrics when shaped on the tyre. The observations were made by means of X-rays, a certain number of threads in the fabric being specially treated with materials opaque to these rays, so as to form reference threads.

Some interesting details regarding the structure of tyre fabrics are given by J. Crompton.[57]

Testing.

Several important points relating to the testing of bleached, dyed and waterproofed yarns and fabrics are given in papers by A. J. Turner,[58] E. A. Fisher,[59] and J. Huebner.[60]

As regards the testing of the fastness of dyeings to light the violet carbon arc is said to give results nearest to those obtained with sunlight.[61] The disadvantages of the mercury arc light have been known for some time.

Faults.

A collection of useful information relating to the cause of defects in dyeing is given by L. L. Lloyd.[62]

The action of formaldehyde in producing discolorations in dyed fabrics is discussed by F. Ristenpart.[63]

In the bleaching of cotton the two most common causes of trouble are oxycellulose and hydrocellulose, and any information on the means of detecting these substances is of considerable value. It has been known for some time that there are different kinds of hydrocellulose and oxycellulose. Hydrocellulose made by the action of sulphuric acid on cotton dyes with Methylene Blue in a similar manner to oxycellulose. It has been shown that this property of the hydrocellulose is due to compounds containing sulphur, most probably sulphonic acids of cellulose, which are not removed by boiling caustic soda solution. E. Knecht and F. P. Thompson[64] give a method for differentiating between this hydrocellulose and oxycellulose, the former having a much greater attraction for Rhodamine B than the latter. The resisting effect of oxycellulose towards direct colours is lost when the material is

[56] *J. Text. Inst.*, 1921, **12**, 418.
[57] *Ibid.*, 1921, **12**, 340, 379.
[58] *Ibid.*, 1921, **12**, 137.
[59] *Ibid.*, 1921, **12**, 197, 252, 337, 385.
[60] *J. Soc. Dyers and Col.*, 1921, **37**, 71 ; *J.*, 1921, 254A.
[61] *J.*, 1921, 149R.
[62] *J. Soc. Dyers and Col.*, 1921, **37**, 101.
[63] *Textilber.*, 1921, **2**, 213 ; *J.*, 1921, 505A.
[64] *J. Soc. Dyers and Col.*, 1921, **37**, 270 ; *J.*, 1921, 841A.

boiled in caustic soda solution, the effect of the hydrocellulose remaining unchanged. From a practical point of view the problem cannot be considered solved at present because the trouble is seldom noticed until the materials have been dyed, and it often happens that alkali is used in the dyebath.

ACIDS, ALKALIS, SALTS, ETC.

By P. Parrish, A.I.C.,

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The heavy chemical industry, during the year under review, has suffered from a financial strain and general depression hitherto unparalleled in its history. At the time of the last review the industry was at the end of a great trade boom, the artificiality of which was singularly apparent. It became clear that the world had not so much healed its wounds as realised its injuries. The reflex of the depression is not so much seen in the paucity of chemical invention as in the limitation of the opportunities for the application of the fruits of research.

Nothing appears to stifle semi-technical experimentation so much as financial strain and uncertainty. Broadly speaking, it is true to say that technical development and progress have been retarded by the acuteness of the depression in question, by the extraordinary state of foreign exchanges, and by the inordinate cost of such basic items as fuel and transport, and (partially) labour.

The effect of the war upon the heavy chemical industry is strikingly dealt with by G. C. Clayton,[1] and it is only necessary to supplement his singularly apposite commentary by remarking that the unprofitable nature of the wet copper extraction process, and the failure to arrive at a suitable returning charge between those concerned, has led to several such works resorting to the combustion of sulphur, or spent oxide, in lieu of cupreous pyrites, in the manufacture of sulphuric acid.

The peculiar position created in the gas industry as regards the value of ammoniacal liquor[2] still remains unsolved. One would have imagined that the situation could have been relieved by the assistance of the ammonia-soda industry to the mutual advantage of both industries. That the peculiar circumstances named have given a fillip to the ammonia-soda industry (to the possible temporary detriment of electrolytic caustic soda processes) cannot be doubted.

[1] *J.*, 1921, 443R.

[2] *Gas World*, 1921, **75**, 587.

Nitrogen Industry.

The department of Scientific and Industrial Research[3] has published a supplement to the original report of the Nitrogen Products Committee, giving statistical information concerning the nitrogen industry during the latter part of the war and down to the end of 1920. These figures reveal that Germany's resources of fixed nitrogen amount to 8830 tons per million of population, as contrasted with 2240 tons per million of our population. Interesting particulars are furnished concerning synthetic nitrogenous fertilisers in Germany.[4] The following annual production figures are given :—Cyanamide, 100,000 tons (fixed nitrogen) ; synthetic ammonia, 300,000 tons ; gas and coke ovens, 100,000 tons : total, 500,000 tons fixed nitrogen.

As an indication that the use of Chile saltpetre is rapidly declining it is shown that, whereas in 1913 770,000 tons was imported, the imports in 1920 were only 40,000 tons.

Intimately connected with the German nitrogen industry[5] is the disastrous explosion which occurred at Oppau on the morning of September 21st, 1921, involving a loss of life variously stated as from four hundred to a thousand, and injuries to one thousand.

The explosion, according to a report of the directors issued on September 23rd and published in the German press during October, originated in a store of 4500 tons of "Ammonsulphatsalpeter." This explanation seems to have been generally accepted. Adverse criticism has, however, been levelled against the investigation work upon which the stability of the material had been decided. Although it is interesting to speculate upon the possible causes of the explosion, nothing but the findings of a Commission of Enquiry of expert technical men is of moment to the chemical industry.

Synthesis of Ammonia.

G. Claude[6] deals with the actual state of the synthesis of ammonia at extremely high pressure, indicating that the compression of the reacting gases from 100 atm. to 900 atm. is effected in one stage by a hyper-compressor capable of dealing with 700 cubic metres of the gases per hour. This quantity suffices for an apparatus rated at a production of 5 tons of ammonia per day. The contact unit comprises four tubes, two in parallel. and then two in series.

By suitable regulation of a continual process for distilling the excess mixture (air) described by W. Lachmann,[7] it is possible to

[3] *J.*, 1921, 287R.
[4] *J.*, 1921, 237R.
[5] *J.*, 1921, 381R. *Times*, Oct. 14-17, 1921.
[6] *Comptes rend.*, 1921, **162**, 442 ; *J.*, 1921, 214A.
[7] U.S.P. 1,363,659 ; *J.*, 1921, 471A.

obtain either nitrogen or oxygen in a pure state from the rectifying column, but not both.

The advantage of a process protected by the Badische Anilin und Soda Fabrik[8] for the manufacture of nitrogen-hydrogen mixture is said to reside in the fact that the gasification periods may be considerably extended; if the water vapour be pre-heated the intercalation of the heating periods may even be entirely dispensed with. The gas mixture may be prepared by introducing air with the steam into a water-gas producer or by mixing with Dowson gas in suitable proportions.

The Claude process is described in detail by J. H. West.[9] In principle, it is similar to the Haber process, but, whereas Haber works at a pressure of 200 atmospheres, Claude uses 900 atmospheres and a temperature of about 600° C. One result of this high compression is that small pipe-work minimises the difficulty of gas-tight joints and valves. The chief advantage of the process, however, is speed and economy in the actual combination. The proportion of combination is much higher at 900 atmospheres than at 200, and therefore the heat produced by the reaction is also higher. In the Haber plant catalyst vessels are of very large size in order to minimise radiation losses, but in the Claude process these vessels are quite small. Comparative efficiencies (expressed as grams of the product per hour per litre-volume occupied by the catalyst) are Haber 350–400 grams, and Claude 5600–6700 grams. The time required to start the Haber plant is three days, whereas the Claude plant will produce ammonia in 4–5 hours, starting all cold. Claude catalyst tubes are of Vicronic, or high tensile alloy (cast solid and bored out), and the basis of the catalyst is peroxidised iron.

In the recovery of the ammonia the Claude process shows advantages over the older process. Under the Haber conditions of 200 atmospheres water is injected into the system, and the ammonia recovered as an aqueous solution. At 900 atmospheres simple water-cooling is sufficient to liquefy the whole of the ammonia with the exception of 2–3%, which can be removed by absorption in sulphuric acid.

L. Duparc and C. Urfer[10] protect a process for the production of catalysts for ammonia synthesis by which a pulverulent mass is produced consisting of a reducing metal (aluminium or magnesium) distributed in a finely-divided and pure state over the oxides of such reducing metals as lithium, uranium, calcium, barium, strontium, titanium, etc. which serve as the carrier. Catalysts produced by this process are said to be highly active and

[8] E.P. 145,058; *J.*, 1921, 508A.

[9] *J.*, 1921, 420R.

[10] E.P. 140,061; *J.*, 1921, 469A.

may be utilised for the synthesis of ammonia at atmospheric pressure and at temperatures between 250°–600° C.

A catalyst for ammonia synthesis and the process of preparing it is described by J. C. Clancy.[11]

A process for the manufacture of catalytic iron, especially free from inhibitive substances, for ammonia synthesis, has been covered by the Nitro-Fixation Syndicate, Ltd., and H. C. Jenkins.[12]

Nitrogen Fixation (Other Methods).

The preparation and properties of calcium cyanamide have been investigated by N. Kameyama.[13] It has been found, *inter alia*, that when calcium cyanamide is prepared by igniting urea with lime, calcium cyanate is formed as an intermediate product at temperatures below 300° C., transformation into cyanamide occurring slowly at 340°–360° C., and rapidly at and above 450° C., and that heating should be of short duration to prevent oxidation of the cyanamide ; 5–7 minutes is adequate.

T. C. Hagemann[14] furnishes details of the power cost in the arc process of nitrogen fixation, showing that the yield per kw.-year amounts to only 115 kg. of fixed nitrogen, as contrasted with 450–500 kg. yielded by the cyanamide process. Graphs are given showing the cost of energy in the arc process as a percentage of the market price, the latter being taken as either £150, £100, or £73 16s. per ton of combined nitrogen. Cheap water power is taken as costing £1 4s. per kw.-year, the average cost of water power is estimated at £2 per kw.-year, and steam-generated power at £3 15s. per kw.-year. At a power cost of £2 6s. per kw.-year, power charges amount to 15% and 20% respectively of the market prices, £150 and £100 per ton of combined nitrogen.

In the arc process for manufacturing calcium nitrate, 15% of the yield is obtained as sodium nitrate, the market price for the combined nitrogen of which is 67% more than that in calcium nitrate.

G. Polysius[15] provides for the lining of calcium cyanamide furnaces with quartzite, cement, or concrete, with or without admixture of cement clinker. No reaction takes place between the charge and the lining, nor does the charge adhere to it.

The Bayerische Stickstoff-Werke A.-G.[16] patent a process and furnace for the production of high-grade crude calcium cyanamide, by which the nitrogen necessary for the reaction is brought into the

[11] U.S.P. 1,363,392-3 ; *J.*, 1921, 469A.
[12] E.P. 159,960 ; *J.*, 1921, 300A.
[13] *J. Coll. Eng. Tokyo Imp. Univ.*, 1920, **10**, 173, 209, 249 ; *J.*, 1920, 818A
[14] *Chem. Trade J.*, 1921, **68**, 170 ; *J.*, 1921, 145A.
[15] G.P. 330,943 ; *J.*, 1921, 259A.
[16] G.P. 396,613 ; *J.*, 1921, 346A.

furnace through channels in the wall. Small charges are arranged together in the furnace and the ignition point is attained simultaneously.

The dissociation pressures of iron nitrides have been calculated by A. A. Noyes and L. B. Smith.[17] From the data they afford no hope is entertained of the direct synthesis of ammonia from iron and nitrogen.

A method for the production of ammonia and ammonium sulphate by the action of steam on cyanogen compounds formed in the distillation of organic nitrogen compounds is patented by F. J. Collin, A.-G. zur Verwertung von Brennstoffen u. Metallen.[18]

T. C. Hagemann[19] gives figures representing the costs for the arc process of nitrogen in order to show that this process is profitable in Norway. Power represents half the running expenses. Calcium nitrate is now being exported from Norway in increasing quantities.

Ammonium Compounds.

A process for the direct production of ammonium chloride from ammonium carbonate has been patented,[20] based on the passage of dry or almost dry hydrogen chloride over dry neutral and/or acid ammonium carbonate, or into solutions containing the same in suspension, with or without ammonium chloride, in addition. After separating the solid product the mother liquor is subjected to treatment with ammonia and carbon dioxide, liberated by the action of the hydrochloric acid on a previous quantity of the material, to produce a fresh suspension of ammonium carbonate.

R. Lessing[21] has found that the impurities which colour commercial ammonium sulphate exist as a fine deposit on the surface of the crystals and that by agitating the product from the saturator with an upward current of slightly acid saturated ammonium sulphate solution at approximately the same temperature as the salt, a white sulphate can be obtained. The dirty solution is filtered, and re-used, the white sulphate being centrifuged and neutralised.

Acid ammonium phosphate is prepared[22] by passing ammonia into a solution of phosphoric acid, sp. gr. 1·26, until the specific gravity reaches 1·28, when acid ammonium phosphate is precipitated.

A process for the production of iron-free ammonia alum has been patented by R. Gans.[23] The purity of the alum prepared by

[17] *Chem. Age*, 1921, **4**, 358; *J.*, 1921, 298A.

[18] G. P. 328,829; *J.*, 1921, 389A.

[19] *Chem. and Met. Eng.*, Mar. 23, 1921; *J.*, 1921, 218R.

[20] Wagenmann, Seybel u. Co., G.P. 323,038; *J.*, 1920, 722A.

[21] E.P. 152,766; *J.*, 1920, 819A.

[22] Gewerkschaft ver. Constantin der Grosse, G.P. 307,093; *J.*, 1921, 45A.

[23] E.P. 132,510; *J.*, 1921, 79A.

this method is of the order of 0·1% of iron referred to the alumina content.

A process for transforming free or combined ammonia into ammonium sulphate has been devised by G. N. Vis.[24] Ammonia (free or combined) with steam and inert gas is absorbed by means of sodium bisulphate practically free from uncombined sulphuric acid to obtain a double sodium ammonium sulphate. The resulting solution is diluted and cooled so as to crystallise out Glauber salts.

An invention of C. Still[25] relates to saturators for producing solid salts by the interaction of gases with liquid, and particularly to ammonium sulphate saturators.

W. Wyld[26] in an interesting article deals with the distillation of ammoniacal liquor, indicating several modifications to the usual type of stills, used both for the release of ammonia from ammoniacal liquor, and for the production of caustic ammonia after the release of carbon dioxide and hydrogen sulphide, etc.

A.-G. für Anilinfabr.[27] prepare powdered ammonium sulphate by spraying through ammonia gas under pressure, solutions of ammonium bisulphate or sulphuric acid.

Further details of the manufacture of ammonium chloride and potassium nitrate are described by Badische Anilin u Soda Fabrik.[28]

To economise the use of fuel in the treatment of ammoniacal liquor J. H. Fairweather[29] concentrates the liquor in a Kestner or other evaporator, releasing most of the free ammonia, which is absorbed in known manner. The residual liquor passes through a heat interchanger back to the gas works circuit, and circulation is continued until the content of fixed ammonia is such as to warrant complete distillation.

G. P. Heisel[30] patents a sulphate of ammonia saturator in which provision is made for the introduction of the ammonia gas by tangential jets in an annular pipe. Thus a vortex motion is set up.

P. Parrish and South Metropolitan Gas Company[31] cover the manufacture of ammonium sulphides by a process which necessitates the maintenance of the liquor in a preliminary still at a specific temperature and pressure.

In a method and apparatus for the recovery of ammonia from ammoniacal liquor, W. C. Holmes and Co., M. Boocock, and W. Wyld[32] provide jackets (to the chambers in which the liquor is

[24] U.S.P. 1,366,301; *J.*, 1921, 147A.
[25] G.P. 328,394; *J.*, 1921, 147A.
[26] *Chem. Age*, 1921, 4, 358; *J.*, 1921, 298A.
[27] G.P. 329,359; *J.*, 1921, 217A.
[28] G.P. 306,334 and 307,112; *J.*, 1921, 179A, 470A.
[29] E.P. 165,833; *J.*, 1921, 582A.
[30] E.P. 166,036; *J.*, 1921, 583A.
[31] E.P. 167,540; *J.*, 1921, 694A.
[32] E.P. 167,719; *J.*, 1921, 694A.

heated and sprayed) through which other gases are passed, and the liquor is preheated by passing it through tubes which traverse the jackets.

A.-G. für Anilinfabr.[33] manufacture solid ammonium chloride by permitting hydrochloric acid gas and ammonia to react in the presence of a fine spray of water. The quantity of the latter is adjusted to absorb, by vaporisation, the heat of reaction, which is thus permitted to proceed to completion.

Nitric Acid and Nitrates.

Details of the ammonia oxidation plant of the Höchst Farbwerke, erected at a cost of about £1,000,000, and having a capacity of 24,000 tons of ammonia, or 140,000 tons of nitric acid, per annum, are described by J. R. Partington.[34] The sources of ammonia in connexion with this plant are:—(1) Synthetic (25–27% NH_3); (2) Concentrated gas liquor (20% NH_3), and (3) cyanamide ammonia liquor (22–27% NH_3). The liquor is rectified in four stills each with a capacity of 20 tons of ammonia per day. Ammonia from gas liquor is scrubbed with caustic soda solution (48°–53° Tw.) and passed through charcoal purifiers, metered through Venturi meters, then driven by centrifugal blowers to the filters and converters. The mixture is maintained at 12·5% NH_3 (by volume). After filtration through eight layers of linen cloth the gas is passed through two central mains to the converter house, whence it is diverted to the 224 converters. The maximum output of each converter is 1·5 tons HNO_3 per 24 hours, the efficiency of oxidation being 89%. The over-all efficiency (including absorption and concentration of weak acid) is 84%. The body of the converter is cast iron and the catalyst a platinum gauze 20 in. in diameter supported on a grid of stout platinum wires. The gases from the converters are passed to four rows of eight absorption towers, each row of towers being provided with twelve coolers of special design. The towers (41 feet high by 21 feet diameter) are of brick and packed with stoneware rings. The internal volume of all towers is equivalent to 81 cub. ft. per lb. NO_2 absorbed per minute. Twenty-five per cent. of the oxides are absorbed as nitrates by saturated sodium carbonate solution fed to the last two towers, and the nitrate is evaporated by waste heat from the converters. The remaining towers are fed with water for the production of nitric acid. The acid from the towers is water-cooled in silicon-iron coolers and received in brickwork stock tanks. The tower acid is concentrated by mixing seven parts of this acid (50% HNO_3) with one part of sulphuric acid, and then de-nitrated.

[33] G.P. 326,619; *J.*, 1921, 178A.

[34] *J.*, 1921, 165R.

Interesting experiments affecting the manufacture of nitric acid by the Schönherr arc process have been made by F. Kodera, I. Kitawaki, and B. Yokohama.[35]

N. C. Hill and H. L. Moyler[36] describe an apparatus for the continuous manufacture of nitric acid. A rotating retort is used, alkali nitrate being introduced midway into a flow of hot sulphuric acid, which gradually merges into a flow of bisulphate. At a point adjacent to that at which the sulphuric acid is introduced, the nitric acid vapours are drawn off.

The Badische Anilin und Soda Fabrik[37] patent a process for catalytic conversion of ammonia into nitrogen oxides. The catalyst in this process consists of copper oxide with a lesser quantity of a compound of lead and manganese containing active oxygen. A yield of 90% of nitrogen oxides is obtained by passing a 7% ammonia-air mixture over the catalyst.

To obviate the formation of ammonium nitrate and ammonium nitrite S. Duparc and C. Urfer[38] patent a method for the direct oxidation of ammonia. A mixture of four volumes of ammonia and seven volumes of oxygen is passed in an undried state at a comparatively high velocity over a catalyst of rhodium black or asbestos containing 3–5% of rhodium, the reacting gases being heated to 500°–650° C. In this way a yield of 97–100% of nitrogen peroxide is obtained.

W. Wyld[39] deals with the use of ammonia oxidation units for sulphuric acid manufacture, suggesting the use of two layers of wire of 0·0125 in. diameter and 120–150-mesh, as contrasted with the usual practice of four layers of 0·065 in. diameter, and 80-mesh, if platinum is to be economised. To obviate rust reaching, or being deposited on the catalyst, it is recommended that lead pipe should be used from the still head to the converter. Precautions are indicated by which disintegration of the asbestos washers is avoided. A 90% efficiency is easily maintained.

A process of concentrating dilute nitric acid has been patented by H. Frischer,[40] by which such dilute nitric acid is introduced to a liquid, unaffected by it, of high boiling point. Phosphoric acid, sulphuric acid, and arsenic acid may be used. The liquid is heated to 140°–160° C., and the nitric vapours are conducted to a dephlegmator.

With an air-ammonia mixture of 8·3% of NH_3 by volume and a catalyst consisting of a mixture of cobaltic and aluminium oxides

[35] *J. Chem. Ind. Tokyo*, 1920, **23**, 1010; *J.*, 1920, 817A.
[36] U.S.P. 1,362,418; *J.*, 1921, 78A.
[37] G.P. 301,362; *J.*, 1921, 79A.
[38] E.P. 133,041; *J.*, 1921, 149A.
[39] *Chem. Age*, 1921, **4**, 150; *J.*, 1921, 177A.
[40] E.P. 137,834; *J.*, 1921, 215A.

in the proportion of 100 parts of cobalt to 2·5–30·0 parts of aluminium, a conversion of 84·5% is obtained by the process of the General Chemical Co.[41] If the catalyst is prepared at a temperature not exceeding 650° C. a conversion as high as 94% is possible.

A patent for the preparation of oxides of nitrogen has been protected by the Badische Anilin u. Soda Fabrik,[42] by which the gas mixture (ammonia-air) preheated to over 400° C. is allowed to come in contact only with (*a*) silica or glazed ware high in silica and (*b*) oxides or carbonates of calcium, magnesium, or aluminium, or a mixture thereof in massive form, before reaching the catalyst, which comprises base metals or their oxides or mixtures or compounds.

A regenerative furnace for the combustion of nitrogen has been patented by Gewerkschaft des Steinkohlenbergwerkes Lothringen and M. Kelting.[43]

The Badische Anilin u. Soda Fabr.[44] cover a process for the production of nitrogen by which producer-gas is burnt with a slight excess of air, pure hydrogen being added to combine with the excess of oxygen, and carbon dioxide and other impurities subsequently eliminated from the gas.

In an article on the concentration of nitric acid, by E. Galle,[45] it is pointed out that the maximum strength of the nitric acid prepared by the oxidation of atmospheric nitrogen or of ammonia is 50% nitric acid. Details of the Pauling tower as improved for this purpose by Hoenig and results of working are given, as also particulars of laboratory experiments showing that, with an effective fractionating column, dilute nitric acid can be concentrated to 65% HNO_3 without the use of sulphuric acid, with no appreciable loss.

A continuous process for the manufacture of concentrated nitric acid is suggested by Bayerische A.-G. f. Chem. u. Landwirtschaftl. Fabrikate, H. Hackl, and H. Bunzel,[46] by the treatment of heated barium nitrate with sulphuric acid in a vessel through which the mixture is conveyed by a screw.

A process for evaporating nitric acid is protected by the Badische Anilin u. Soda Fabrik[47] by which acid is passed over heated metallic surfaces or bodies at a temperature of 180°–250° C., in such a way that the liquid is kept from contact with these by a layer of vapour.

[41] E.P. 136,158; *J.*, 1921, 258A.
[42] G.P. 303,331 and 307,001; *J.*, 1921, 300A.
[43] G.P. 331,488; *J.*, 1921, 300A.
[44] G.P. 306,302; *J.*, 1921, 302A.
[45] *Z. angew. Chem.*, 1921, **34**, 168, 173; *J.*, 1921, 385A.
[46] G.P. 307,601; *J.*, 1921, 432A.
[47] G.P. 335,762; *J.*, 1921, 508A.

Porous ferric hydroxide or antimony oxide or a mixture of these under pressure and at low temperature, if desired, is used by the Badische Anilin u. Soda Fabrik[48] as a catalytic medium for the conversion of the lower oxides of nitrogen into the higher oxides.

The manufacture of nitric acid from the air by the explosion method is described by F. Häusser.[49]

J. R. Partington[50] protects a process for the oxidation of ammonia, whereby ammonia and steam are mixed in the presence of oxygen, and the preheated mixture is passed over a heated catalyst.

A process for concentrating nitric acid is described by H. Frischer.[51]

A. R. Frank and N. Caro[52] protect processes of ammonia oxidation, in which (*a*) the contact agent forms a resistance in an electric circuit, and is thereby heated uniformly, or (*b*) the contact agent is constituted of metallic gauze.

H. W. Webb[53] communicates interesting information concerning an investigation made to determine the effect of individual variables by altering only one variable in any particular set of experiments. The results show mainly that working in glass apparatus with sodium nitrate : acid ratio of 1 : 1·1 by weight, decreasing the acid strength from 97% to 85% (thus decreasing the molecular ratio of acid, and increasing the water present in the system), the yields of nitrogen in all forms increased about 1·5% to a maximum of 98·7%, although very little difference in yield was found between strengths of from 93% to 85% H_2SO_4. The losses of nitrogen, which existed mainly in the nitre cake, fell from 0·5% to zero. Working on a small-scale works plant the results confirmed those obtained in the laboratory, although the actual nitric acid yield fell off from 5% for the 96% acid to about 2·5% for acid of 92% strength. The nitrogen recovery, all forms, was as high as that experienced in the laboratory experiments. Using the acid of optimum strength 91% as shown above, and varying the weight ratio from 1 $NaNO_3$: 1·11 H_2SO_4 to 1 $NaNO_3$: 0·934 H_2SO_4, no marked difference was obtained in the nitric acid recovered or of nitrogen, all forms, which were 97·5%–98%, and 97·8%–98·6% respectively when working in glass in the laboratory. The same conditions on the small-scale works plant with 92% strength, however, gave a marked difference in the nitrogen yield, which fell off appreciably with a decrease in the ratio of sulphuric acid, from approximately 98% to 94·7%, and yield of nitric acid

[48] G.P. 335,910 ; *J.*, 1921, 508A.
[49] *Stahl u. Eisen*, 1921, **41**, 956; 999 ; *J.*, 1921, 580A.
[50] U.S.P. 1,378,271 ; *J.*, 1921, 583A.
[51] G.P. 307,613 and 303,271 ; *J.*, 1921, 623A.
[52] G.P. 303,824 and 304,269 ; *J.*, 1921, 623A.
[53] *J.*, 1921, 212T.

of from 95·8% to 90·6%. The reason for these low results was traced to the action of the iron of the retort, which was attacked, much iron being found in the nitre-cake.

An investigation by H. W. Webb[54] of the effect of the presence of chlorine and hydrochloric on the absorption of nitrous gas has shown that when a mixture of chlorine and nitrogen peroxide diluted with air is passed through a series of absorption towers, there is a point where nitrogen peroxide is rapidly absorbed with the formation of an acid containing 55–60% HNO_3 and very little chlorine. Tests were carried out on a series of eight towers (counter-current principle) with varying rates of water feed. From the results it was noticed that a sudden rise in concentration took place when the acid attained a concentration of 35–40% HNO_3, and that this coincided with the greatest decrease in chlorine content. The tower in which this occurred varied with the rate of water feed.

The influence of chlorine on the absorption of nitrous gases is explained as follows: At approximately 54% HNO_3. nitric acid contains only combined water ($HNO_3.2H_2O$) and the reaction $HNO_3+3HCl \rightarrow NOCl+Cl_2+2H_2O$ takes place only with acid above this strength. The main reaction in the first towers is the conversion of the hydrochloric into nitrosyl chloride and chlorine, but when the gases meet with acid containing free water the following reactions commence: (1) $NOCl+H_2O \rightarrow HNO_2+HCl$; (2) $Cl_2+H_2O \rightarrow HClO+HCl$; (3) $HNO_2+HClO \rightarrow HNO_3+HCl$. The chlorine thus oxidises nitrous acid (formed from the nitrosyl chloride) and also accelerates the conversion of nitrogen peroxide to nitric acid by oxidising the nitrous acid formed by the reaction between nitrogen peroxide and water, and by displacing equilibrium, causing a more rapid absorption of nitrogen peroxide. Reactions 1, 2 and 3 proceed rapidly until the nitric acid content is such that no free water is present, then the reaction $HNO_3+3HCl \rightarrow NOCl+Cl_2+2H_2O$ takes place.

A method for the prevention of nitrogen losses in the oxidation of ammonia is protected by H. Frischer.[55]

Aluminium and Compounds.

To facilitate the precipitation of iron from aluminium sulphate solution by the addition of a potassium salt and 5–10% excess of alumina (E.P. 9148 of 1914) the addition of impalpable mud of ground silicious residues from the treatment of aluminous minerals or native alunite is suggested by[56] P. Spence and Sons, Ltd., H.

[54] *J.*, 1921, 163T, 212T.
[55] G.P. 301,681; *J.*, 1921, 694A.
[56] E.P. 161,606; *J.*, 1921, 389A.

Spence, and W. B. Llewellyn. This process admits of ready separation of basic ferric potassium sulphate.

R. H. Tingley[57] describes the alunite deposits in the Tushar Mountains, Marysvale, Utah, where the mineral ($K_2O,3Al_2O_3,4SO_3,6H_2O$) contains 37% of aluminium oxide. It is said that the Tushar deposits resemble those at Tolfa, Italy. The view is expressed that these deposits will afford sufficient alumina, as well as potash, to meet all American requirements.

For the manufacture of alum and aluminium sulphates, A. Matheson[58] proposes to heat alunite to 700°–900° C. in a furnace having superposed hearths. Sulphur gases from the furnace pass into a chamber at 400°–500° C. containing a portion of the roasted ore. Sufficient water is added to form sulphuric acid. After treatment with the gases the product is lixiviated to recover alum and aluminium sulphate.

J. Coggin Brown[59] contributes an article having reference to the occurrence and exploitation of bauxite in India.

Argon and Other Rare Gases.

According to a patent by E. Barbet et Fils et Cie.[60] liquid argon, containing small quantities of nitrogen, is drawn from an air-rectifying plant and vaporised in a plate rectifying column, by means of a coil containing cold gaseous nitrogen. The vapours are passed through a condenser immersed in liquid nitrogen, and the liquid argon so obtained is returned to the top of the column, while uncondensed vapours pass back into the air rectifier. Another fraction from the air rectifier containing neon and helium, with some hydrogen and nitrogen, is cooled, compressed, and then fractionally evaporated so that liquid nitrogen separates, while neon, helium, and nitrogen are vaporised. These gases are then cooled to such an extent that neon is liquefied and drawn off. The helium is separated from hydrogen by passage over wood charcoal.

Xenon and krypton, drawn off from the bottom of the air rectifier, are separated by a similar process of evaporation.

Arsenic.

It has been found[61] that delicate and precise adjustment of the draught, and efficient and quick cooling, are essential if a pure, dense arsenic trioxide is to be recovered from the blast-furnace flue dust and Cottrell plant dust. The cooling chambers should be deep, and their width should increase as they leave the furnace.

[57] *Air Mag.*, Oct., 1921 ; *J.*, 1921, 407R.
[58] E.P. 167,555 ; J., 1921, 694A.
[59] *J. of Ind. and Lab.* ; *J.*, 1921, 195R.
[60] E.P. 129,989 ; *J.*, 1921, 147A.
[61] E. C. Williams, *Eng. and Min. J.*, 1920, **110**, 671 ; *J.*, 1920, 747A.

Bromine.

In Germany the production of bromine increased from 7500 kg. in 1867 to 866,000 kg. in 1911, and during the same period the production in America was augmented from 5000 kg. to 3,236,000 kg. W. Hüttner,[62] in a description of the methods used for the manufacture of bromine, indicates that the general process consists in the decomposition of bromides by chlorine, but in a few works, he observes, the electrolytic process is employed.

Calcium Salts.

Fused calcium chloride is manufactured[63] by the passage of hydrochloric acid gas, or waste gas containing it, through a tower packed with lumps of calcium carbonate. The heat of reaction concentrates the solution of calcium chloride as it descends the tower, and such liquor which collects at the bottom solidifies on cooling.

L. Roon[64] patents a process for the manufacture of calcium carbonate by the atomisation of milk of lime, and the reaction of carbon dioxide with the resulting mist.

Carbon.

The development of gas warfare has resulted in an immense advance of knowledge in the preparation of activated and decolorising carbon; indeed, the subject has been rescued from the state of general empiricism in which it had hitherto reposed.

E. G. R. Ardagh[65] has contributed a paper on the subject, in which the main conclusions of the American workers, N. K. Chaney and F. W. Zerban, associated with the U.S. Chemical Warfare Service, and other State departments, are confirmed by independent experiments. He also suggests other aspects of the problems of preparation which have arisen during his experiments.

It is firmly established that activation is promoted by: (*a*) the use of nitrogenous carbonaceous material, or (*b*) one containing lime or silica, natural or impregnated; (*c*) high temperature and prolonged treating; (*d*) extracting the impregnating materials from the carbonised product to improve capillarity; (*e*) fine grinding to give large contact area. No mention is made of carbonisation under moderate or high vacua. Based upon N. K. Chaney's hypothesis the successful preparation of active carbon from anthracite as a raw material was made possible. The paper contains references mainly dated from 1918, upon which much of

[62] *Chem.-Zeit.*, 1921, **45**, 49; *J.*, 1921, 115A.
[63] A. Riedel, G.P. 327,867; *J.*, 1921, 179A.
[64] U.S.P. 1,372,193; *J.*, 1921, 346A.
[65] *J.*, 1921, 231T.

the paper has been ably constructed; undoubtedly the references themselves form a valuable bibliography of the subject.

An article on the absorptive power of charcoal is contributed by H. Herbst,[66] wherein it is suggested that this depends partly on the content of pure amorphous carbon, and can in some cases be increased by removing tarry impurities by means of a solvent, or by distillation, or by destroying by chemical means as in the Aussig zinc process.

F. C. Dyche-Teague[67] protects a process for the production of pure carbon by which carbon monoxide produced by the passage of carbon dioxide (arising in a subsequent stage of the process) through coke in a gas-fired retort, is decomposed into carbon and carbon dioxide by catalytic action. The carbon deposit and catalyst are separated by a magnetic field or by gravitation.

Chromium and Salts.

It is stated[68] that chromium ore has been mined at several localities in New Caledonia, but that the richest and most productive mine is that of the Tiebaghi Mine, Paagonmene. Exports in 1920 were 91,536 metric tons, of which the Tiebaghi Mine furnished 74,317 tons.

Reference is made[69] to the chromium deposit at Raotina, near Skoplje, along the Vardar River, and at Dubostica, in Bosnia. Apparently the Germans took advantage of the deposits during the war, recovering in the former case about 150 tons per day.

A process for the conversion of chromate and bichromate of sodium or potassium into chromium sulphate is described by F. M. Mooney.[70] A solution containing chromium trioxide is cooled to crystallise Glauber's salt, and after separation of the crystals, sulphur dioxide is passed through for effecting the reduction.

Copper Sulphate.

R. E. Bea[71] converts copper waste into crystals of copper sulphate by suspending in dilute sulphuric acid a perforated receptacle containing the copper waste (into which dips a leaden anode), and a porous pot filled with dilute sulphuric acid in which hangs a leaden cathode. By this arrangement the deposition of copper on the leaden cathode is obviated.

[66] *Biochem. Zeits.*, 1921, **115**, 207; *J.*, 1921, 388A.
[67] G.P. 160,561; *J.*, 1921, 347A.
[68] *J.*, 1921, 411R.
[69] *U.S. Com. Rep.*, 29. 12. 1920; *J.*, 1921, 91R.
[70] U.S.P. 1,379,578; *J.*, 1921, 544A.
[71] E.P. 147,689; *J.*, 1921, 178A.

Formic and Acetic Acids, Etc.

M. Enderli[72] protects a process for the manufacture of sodium formate by treatment of sodium sulphate with carbon monoxide in the presence of milk of lime. The dilution of the sodium sulphate exerts considerable influence on the reaction.

Interesting details concerning the manufacture of acetic acid, and the extensive developments which have taken place of recent years, are described.[73] Reference is made to acetic acid from pyroligneous acid, and it is indicated that importance attaches to the methyl alcohol produced from pyroligneous acid. The probability of methyl alcohol bearing the expenses incurred in selling the acetic acid at "cut" prices, in order to meet competition from the synthetic product, is foreshadowed. For this reason it is concluded that the synthetic acid must be sold at a figure below present market values if an economical struggle with the wood distillation product is contemplated. The stages in the production of acetic acid from calcium carbide, *viz.*: (*a*) The generation of acetylene and its purification; (*b*) the catalytic hydration of acetylene to form acetaldehyde; and (*c*) the oxidation of the latter to acetic acid, are described in some detail, and finally an indication is given as to the outlook for synthetic acid.

Haloids.

The manufacture of chlorates, bromates, and iodates is covered by a patent of H. Schulz.[74] A high yield of chlorates is obtained when halogens and air at atmospheric or increased pressure are passed into an aqueous suspension of any suitable oxide or hydroxide in the presence of a catalyst, such as manganese dioxide. Alternatively air may be passed into a solution in which the catalyst is suspended and in which a halogen is being generated. In the absence of the use of air or a catalyst only a 16% conversion is possible.

Hydrochloric Acid.

T. L. Bailey[75] indicates that inferior fuel has been responsible for inefficient distribution of heat in saltcake furnaces and pots. To remedy this and to eliminate smoke a supply of preheated tertiary air has been admitted to the fire through a 4-in. cast-iron pipe at such a point as to secure the necessary indraught of air.

The utilisation of hydrochloric acid in lieu of sulphuric acid is suggested by H. Hackl[76] for the treatment of crude phosphate,

[72] E.P. 165,163; *J.*, 1921, 583A.
[73] *J.*, 1921, 345R.
[74] G.P. 328,211; *J.*, 1921, 147A.
[75] *J.*, 1921, 279R.
[76] *Chem.-Zeit.*, 1921, **45**, 149; *J.*, 1921, 177A.

dicalcium phosphate being subsequently precipitated by means of milk of lime.

A new method for the purification of hydrochloric acid is indicated by J. Lamquet,[77] by which arsenic, chlorine, and sulphur dioxide can be removed from commercial hydrochloric acid by the simple addition of hypophosphorous acid or one of its salts, the reactions being represented thus :—

$$3H_3PO_2+4AsCl_3+6H_2O=3HP_3O_4+12HCl+4As.$$
$$H_3PO_2+2Cl_2+2H_2O=H_3PO_4+4HCl. \qquad H_3PO_2+SO_2=H_3PO_4+S.$$

By using the barium salt, sulphuric acid is precipitated at the same time.

Hydrogen.

The extension of synthetic ammonia production, and also of hydrogenation generally has demanded detailed investigation into existing, and possible, methods of hydrogen production.

A very comprehensive review of existing practice, and possible developments is given by E. K. Rideal[78]: "Although industrial uses of hydrogen admit of a wide variation in inherent purity, so far as the basic principles of production are concerned, steam-iron and water-gas catalytic processes predominate, electrolytic methods being dependent upon the hydrogen evolved as a by-product in electro-chemical processes."

Developments in the steam-iron process centre around an increase in the reduction mass conversion, $Fe \rightarrow Fe_3O_4$, which at present only attains 1%. Activated reduction masses, *i.e.*, FeMn, FeCu, whilst giving better yields initially, are susceptible to irreversible poisoning, and an independent line of investigation consists in increasing the mass contact area by projecting the finely-divided mass at either stage into the gas zone.

The consumption of steam, and therefore of heat, during the steaming phase, leaves much to be desired; this exceeds the theoretical quantity by as much as ten times. Additional studies of the system, hydrogen-water-iron-iron oxides, in conjunction with those of the water-gas reaction, are necessary to determine the optimum conditions favourable to water-gas economy during the reducing process. In this connexion the conditions admitting of the utilisation of carbon monoxide with or without plant alterations have possibilities.

For the purification of the hydrogen by this process, general methods are available for carbon dioxide and hydrogen sulphide. A suitable treatment for the removal of thiophen and carbon bisulphide exists in the nickel catalytic process of Carpenter and

[77] *Bull. Soc. Chim. Belg.*, 1920, **29**, 309; *J.*, 1921, 431A.
[78] *J.*, 1921, 10T.

Evans, at present successfully operating on coal-gas, but which would require modification for gaseous mixtures of high carbon monoxide content. Another method, hydrolytic in character, in which a carefully prepared iron oxide-aluminium catalyst is used is available. The two processes differ as follows :—(1) $CS_2+2H_2=C+2H_2S$; (2) $CS_2+2H_2O=CO_2+2H_2S$.

The removal of hydrogen sulphide by selective combustion over iron oxide with or without promoters, has possibilities, but it is not without disadvantages, certain side reactions and even reversibility interfering with the smooth working of the process. Iron hydroxide as a suspension in a liquid medium is also available.

In spite of the comparative inactivity of carbon monoxide purification from this gas by direct absorptive methods is being developed. Selective combustion with oxygen and utilisation of the water-gas reaction, are other independent processes. Selective combustion has worked very smoothly on units of 1000 cub. ft. of hydrogen per hour.

Production of Hydrogen by the Water-gas Catalytic Process.

This process is already exceedingly promising. The present stage of development of the Mond and Langer process by the Badische Co. gives hydrogen for a steam and water-gas consumption which is much lower than that experienced by the steam-iron processes.

Direct Production of Hydrogen from Coke.

The ideality of a continuous process of making hydrogen from coke based upon the water-gas reaction, $C+2H_2O=CO_2+2H_2$ does not seem easy of attainment, principally because the reactions seem to be amenable only to catalytic stimulation, and the ash content of coke, which in itself has a marked catalytic effect, may vary between wide limits.

By alternate oxidation and reduction of iron W. Paternoster[79] covers a process for the production of hydrogen.

A. J. Hale[80] deals fully with the recent developments in the electrolytic production of hydrogen and oxygen. A description of non-diaphragm and diaphragm cells is given, cost and lay-out of plant are indicated, and the conviction is expressed that electrolytic production of hydrogen and oxygen has a considerable future before it.

G. F. Jaubert[81] has patented the manufacture of hydrogen from silicon and its alloys. The phosphide content in powdered ferrosilicon is decomposed by the addition of sufficient water to produce

[79] G.P. 328,691 ; *J.*, 1921, 179A.

[80] *J.*, 1921, 123R.

[81] U.S.P. 1,366,185 ; *J.*, 1921, 148A.

a pasty mass, which is then added to a solution of caustic alkali in a hydrogen generator.

Gases from blast furnaces and electrolytic smelting furnaces are treated, according to C. Toniolo and Officine Elettrochim. Rossi,[82] with steam in the presence of a catalyst, such as iron oxide, with or without an alkali-metal oxide, chromium oxide, or an alkaline-earth oxide, and the hydrogen or hydrogen and nitrogen mixture is freed from carbon monoxide, carbon dioxide, and steam by suitable methods.

G. Claude[83] deals with the manufacture of hydrogen for the synthesis of ammonia, the sources suggested being town gas or coke-oven gas. Solvents under pressure are recommended for the separation of hydrogen and carbon monoxide.

E. B. Maxted[84] describes a complete unit for the production of hydrogen, and its utilisation for hydrogenation. As regards hydrogen production such simple processes as electrolysis of aqueous solution and the cyclic water-gas process are favoured, the latter process being described. The use of reinforced concrete has considerably cheapened the cost of the purifier section of the plants. Hydrogen of high purity is furnished with very little skilled control.

Hypochlorites.

E. Sidler[85] covers a process and apparatus for the manufacture of bleaching powder. The chlorinating chamber resembles a metallurgical burner, except that the shelves are in the form of plates, with a central shaft and arms provided with rabbles. The lime and chlorine pass in the same direction.

A. Pfülf[86] has devised a shaft-shaped chamber provided with various devices for promoting increased contact and for facilitating interaction between lime and chlorine.

A process for reducing calcium hypochlorite to a form suitable for compression into pastilles, balls, or cubes, is protected by Chem. Fabr. Griesheim-Elektron,[87] by using sodium chloride specially purified from magnesium chloride; the product is stated to be of much wider application than the usual form of bleaching powder.

Iron Salts.

F. Brandenburg[88] patents a process for decomposing salts in pans in the working of spent pickle liquor to ferric oxide. Previously-

[82] E.P. 152,975; *J.*, 1921, 148A.
[83] *Comptes rend.*, 1921, **172**, 974; *J.*, 1921, 387A.
[84] *J.*, 1921, 279R.
[85] G.P. 329,178; *J.*, 1921, 216A.
[86] G.P. 329,844; *J.*, 1921, 301A.
[87] G.P. 338,117; *J.*, 1921, 695A.
[88] G.P. 324,259; *J.*, 1921, 115A

made ferric oxide is charged into the decomposing vessel, which is heated, and spent liquor is then added gradually and continuously, with constant stirring. A similar process is applicable to the treatment of waste liquors containing ferrous sulphate, magnesium chloride, sodium bisulphate, etc.

Reversible reactions of carbon monoxide with iron oxides have been investigated by G. Chaudron.[89] Ferric oxide is reduced to the magnetic oxide by carbon monoxide. Temperature thus influences the equilibrium. Below 580° C. there is a single system corresponding to $Fe_3O_4+4CO \rightleftarrows 3Fe+4CO_2$. Above 580° C. there are two equilibria before arriving at Fe, viz., $Fe_3O_4+CO \rightleftarrows 3FeO+CO_2$ and $FeO+CO \rightleftarrows Fe+CO_2$. Below 580° C. ferrous oxide is unstable and is transformed into a mixture of Fe and the magnetic oxide $4FeO \rightarrow Fe_3O_4+Fe$.

Magnesite.

In view of the extraordinary demand for this mineral, many developments are taking place in Austria, the most important mines belong to the Veitscher Magnesitwerke in Styria.[90] During 1913, 123,900 tons of calcined mineral was exported, and in 1920 about 63,000 tons.

Nitre Cake.

A contribution by H. T. Calvert and E. H. Norris[91] deals comprehensively with the production and consumption, uses, distribution, and use in other countries, etc. of nitre cake during the war period, 1915–1919. When the estimated pre-war production of nitre-cake, namely 2000 tons per month, is contrasted with the rate at which nitre-cake was being utilised at the end of 1917, namely 24,000 tons per month, the importance and value of the work of the late Acid Supplies Branch of the Explosives Department of the Ministry of Munitions are appreciated. The development and extension of the use of nitre-cake, it is stated, saved the erection of Government acid plant capable of a production rated at 8000 tons of 100% sulphuric acid per month.

A concise review of the methods suggested for the complete utilisation of nitre cake is given by W. H. H. Norris.[92] Interesting particulars are furnished of a suitable process worked out by the author in conjunction with H. S. Denny and C. W. Bailey for ammonia absorption by which sulphuric acid is entirely dispensed with. An illustration of the plant and costs of the process are

[89] *Comptes rend.*, 1921, **172**, 152 ; *J.*, 1921, 146A.
[90] *Times Trade Suppl.*, 14. 5. 21 ; *J.*, 1921, 196R.
[91] *J.*, 1921, 407R.
[92] *J.*, 1921, 208T.

given, in addition to details of a nitre-cake granulation plant, method of operation, and cost of granulating such cake.

PERMANGANATES.

The effect of temperature, current density, and concentration of the alkali upon the production of sodium permanganate has been studied by C. O. Hanke and O. W. Brown,[93] using an anode containing 92% of manganese. The presence of a diaphragm is not necessary if calcium hydroxide is added to the electrolyte in excess. The calcium hydroxide apparently forms a film over the cathode which serves as a diaphragm.

PHOSPHORIC ACID AND PHOSPHATES.

Interesting large-scale experiments in the production of phosphoric acid from phosphate rock by smelting the latter in a fuel-fed furnace, giving a 90% yield, are described by W. H. Waggaman and T. B. Turley.[94] It is estimated that the cost of phosphoric acid by this process will be $49·83 as contrasted with $81·25 when produced as acid phosphate (superphosphate) by the sulphuric acid process.

W. F. Hillebrand and G. E. F. Lundell[95] contribute an article on the volatilisation losses of phosphorus during the evaporation of phosphates with sulphuric acid or fusion with pyrosulphate.

Strongly heating a mixture of crushed phosphate rock with sand and coke is a process patented by W. H. Allen[96] for the manufacture of phosphoric acid.

The concentration of phosphoric acid by spray evaporation is dealt with by H. E. La Bour,[97] who points out that the difficulties incidental to the evaporation of phosphoric acid, by reason of the formation of scale from sludge and metaphosphate deposited on the heating surfaces, are avoided. The Chem. Fabr. Marienfelde[98] protect a process for the manufacture of a solid, non-hygroscopic form of phosphoric acid in which starch paste is added to dilute phosphoric acid and stirred at 15°–20° C. The mixture is then dehydrated *in vacuo* or in a current of air at 30° C. The product obtained may contain up to 25% of free phosphoric acid and may be used as a substitute for tartaric acid in baking powder etc. Interesting information and statistics concerning the phosphate industry, the sources of supply of mineral phosphate, and the

[93] *J. Phys. Chem.*, 1920, **24**, 608; *J.*, 1921, 78A.
[94] *Chem. and Met. Eng.*, 1920, **23**, 1057; *J.*, 1921. 77A.
[95] *J. Amer. Chem. Soc.*, 1920, **42**, 2609; *J.*, 1921, 78A.
[96] U.S.P. 1,368,379; *J.*, 1921, 215A.
[97] *Chem. and Met. Eng.*, 1921, **24**, 466; *J.*, 1921, 215A.
[98] G.P. 335,474; *J.*, 1921, 508A.

manufacture of superphosphate are given by W. Packard.[99] It is stated that reliable estimates of the world's output of superphosphates are difficult to obtain, but it may be assumed that in 1913, seven million tons of phosphate rock was acidified, producing over twelve million tons of superphosphate. The following figures may be regarded as the approximate annual production of the principal countries:—America, 3,000,000 tons; France, 1,800,000 tons; Germany, 1,500,000 tons; Great Britain, 900,000 tons: total, 7,200,000 tons.

Dealing with the aspect of reverted and insoluble phosphate, as contrasted with superphosphate, the only form of water-soluble phosphate, the view is affirmed that the demand of the latter is not likely to suffer, if for no other reason than that a quick return is afforded for the money expended.

Soda and Potash Salts.

Max Muspratt[100] announces that the Leblanc process has been superseded by the electrolytic process.

An interesting article dealing with the chemical efficiency and concentration of caustic soda and salt from the Townsend electrolytic cell is contributed by A. H. Hooker.[101] A description of the Niagara Falls plant is given. This plant produces 65 tons of caustic soda and 60 tons of chlorine daily. The most recent type of cell in use is of 4000 amps. capacity. The electrochemical efficiency is 96–97%, using a high current density of 100 amps. per square foot of cathode, at slightly over 4 volts per cell. The caustic soda concentration is 125 g. per litre.

Interesting particulars concerning electrolytic diaphragm cells for the production of alkali and chlorine are furnished by H. K. Moore.[102]

A project for the production of sodium carbonate is under the consideration of the Soda Mines and Products Company at Sodalake[103] in British Columbia. The waters of this lake contain 6% of sodium carbonate.

A process of some interest as affecting the manufacture of potassium sulphate and hydrochloric acid has been patented by the Fabrique de Produits Chimiques de Thann et de Mulhouse.[104] Potassium chloride in a finely-powdered state is treated with sulphuric acid of such strength (70–72% H_2SO_4) as to render the moist mixture as pulverulent as possible. The mixture has to be

[99] *J.*, 1921, 288R, 304R.
[100] *J.*, 1921, 155R.
[101] *Chem. and Met. Eng.*, 1920, **23**, 961; *J.*, 1921, 7A.
[102] *Ibid.*, 1920, **23**, 1011, 1072, 1125; *J.*, 1921, 77A.
[103] *J.*, 1921, 107R.
[104] E.P. 137,529; *J.*, 1921, 689A.

heated in three stages, and a slight excess of sulphuric acid used to ensure the production of potassium sulphate, free, or almost free, from chloride. The three stages necessitate stirring at respective temperatures of 100°–120° C., 300° C., and finally 800° C. Sulphuric acid may be replaced by potassium bisulphate. Presumably, experience of the operation of this process has led to some modification or improvement, as is evidenced by an additional patent,[105] indicating that the foregoing three stages of desiccation may be conducted progressively in a single furnace, provided care is taken to maintain the mass solid and porous. It is suggested that aqueous sulphuric acid containing more than 70–72% of SO_3 may be used, the pulverulent nature of the mixture determining the proportions.

In the manufacture of ammonia-soda J. Delmar[106] patents a process by which the lime for the regeneration of ammonia from ammonium chloride liquors is converted into calcium cyanamide, before being used in the process. Thus, further quantities of ammonia and carbon dioxide are developed which are utilised in the first stage of the process.

An apparatus by which salt can be profitably manufactured from sea water is suggested by T. A. Reid.[107]

The Schweizerische Soda-Fabr.[108] have devised a process for the causticisation of soda in the cold. A mixture of sodium carbonate solution and lime is treated in a sort of centrifugal machine. Interaction is hastened and is completed without heat, 10 cub. m. of liquor being causticised in 10 minutes.

According to a protected ammonia-soda process by J. H. McMahon[109] water-gas is separated into hydrogen and carbon monoxide. The hydrogen is used for the production of synthetic ammonia, which is absorbed in a solution of common salt, whilst the carbon monoxide is converted to carbon dioxide which is used in carbonating towers.

H. Voss[110] deals with the heat balance of the ammonia-soda process, and concludes that the excess of sodium chloride used in the reaction, the residual calcium chloride, the heat expended in recovering ammonia from waste liquor (which it is stated is two or three times the calculated amount) and the heat losses in radiation, conduction, and cooling in various parts of the system constitute the principal thermal losses of the process.

It is pointed out[111] that the only potash-producing area now

[105] E.P. 154,111 ; *J.*, 1921, 44A.
[106] G.P. 333,748 ; *J.*, 1921, 347A.
[107] E.P. 159,592 ; *J.*, 1921, 300A.
[108] G.P. 332,003 ; *J.*, 1921, 301A.
[109] U.S.P. 1,384,141 ; *J.*, 1921, 623A.
[110] *Chem.-Zeit.*, 1921, **45**, 940, 968 ; *J.*, 1921, 767A.
[111] *J.*, 1921, 351R.

under German control is that of central Germany, where conditions of production are favourable. In 1920, with an output of 11,390,000 metric tons of potash, the pre-war level was almost attained, viz., 11,607,510 in 1913. Sales, it is stated, have declined, and although the extent to which English, Belgian, French, Russian, Austrian, and other markets have been lost cannot be ascertained, the view is expressed that the acquisition of Alsace by France has broken the German world monopoly of potash. The increase in the exports of potash (K_2O) from Alsace between 1913 and 1920 is shown in the appended table :—

	1913.	1919.	1920.
		Metric tons.	
France	10,278	48,958	86,578
Germany	13,743	13,743	13,743
United States	12,185	26,702	55,967
Great Britain	219	4499	17,890
Belgium	614	4414	19,750
Other Countries	3682	9157	18,990
	40,721	107,473	212,918

The deleterious action of potassium nitrate on a melting pot used for the manufacture of nitrite from nitrate by means of lead is described by A. Lottermoser.[112]

J. W. Turrentine and F. S. Shoaff[113] describe a continuous counter-current method of leaching potash from kelp from which an extraction of 97–99% is obtained.

Sulphuric Acid.

A valuable contribution by H. J. Bailey[114] is furnished replete with statistics relative to the production and utilisation of sulphuric acid, sulphur, pyrites, pyrites cinders, spent oxide, imported sulphur, sulphuric acid from chamber plants, oleum, the consumption of sulphuric acid for explosives manufacture, the production of nitric and hydrochloric acids, and nitre cake, and particulars affecting superphosphate and compound manures, basic slag, sulphate of ammonia, and concentrated liquor. Much valuable information concerning the manufacture of sulphuric acid in the United States is furnished in Bulletin 184,[115] issued by the U.S. Bureau of Mines. In 1865 only 37,500 tons of 100% sulphuric acid was manufactured. In 1900 this had become over one million tons. It is now estimated that the normal requirements of sulphuric acid of the United States are equivalent to about 3½ million tons,

[112] *Chem.-Zeit.*, 1921, **45**, 581 ; *J.*, 1921, 507A.
[113] *J. Ind. Eng. Chem.*, 1921, **13**, 695 ; *J.*, 1921, 656A.
[114] *J.*, 1921, 246R.
[115] *J.*, 1921, 101R.

of which approximately one-half is required for superphosphate manufacture.

Evidence of the influence of the war is afforded by reference to the subjoined table, demonstrating the changes of the various sources of sulphur as raw material :—

	Percentage of total quantity.		
	1914.	1917.	1918.
Brimstone	2·6	32·6	48·0
Pyrites (Spanish)	50·0	22·9	7·6
„ (domestic)	15·8	11·8	12·7
„ (Canadian)	7·9	6·9	7·5
Zinc ores	13·2	18·1	16·1
Waste gas from copper smelters	10·5	7·7	8·1
	100·0	100·0	100·0

The bulk of the brimstone is obtained by the Frasch process. Brimstone is reported as being more valuable than 40% pyrites to the extent of 3–4 cents per unit, assuming the pyrites cinders are valueless to the acid-maker.

Increasing attention is being given to the recovery of pyrites from waste coal, of which 1½ million tons, having a 40% sulphur content, could be produced by the Eastern States.

Large quantities of sulphuric acid are produced at the zinc works, although there are still some works which fail to utilise the sulphurous gases. At the copper works large acid plants are to be found, notably at the works of the Tennessee Copper Company.

Sulphur combustion plant is usually of a continuous character. The Tromblee and Paul rotary and the Vesuvius vertical burners are largely used. Pyrites fine burners are principally confined to the Herreshoff and Wedge types, and the Hegeler, Spirlet, and Wedge (muffled) furnaces are used for zinc ores.

As an eliminator of dust from burner gases and as an arrester of acid mist from acid concentration plants, the Cottrell electrical precipitator has found favour and is giving satisfaction.

Increasing attention is being given to intermediate towers; indeed, the "Anaconda packed cell" system—a type of packed tower with special filling—is reported as being used in lieu of chambers. Concentrators of the silica basin, modified Kessler, and Kalbperry types, are principally used. The Mannheim, Badische, Grillo-Schroeder, and Tentelew contact systems are all in use. Descriptions and comparisons of the various types of SO_2 coolers, filters, drying and absorbing systems, and methods of preparing and revivifying catalysts are given.

It is interesting to have details of the manufacture of sulphuric acid by the chamber process under tropical conditions. Singularly little information has hitherto been published in this connexion.

W. H. Maudsley[116] describes a plant at Mount Morgan, comprising seven chambers with an aggregate capacity of 119,643 cub. ft., one Glover, 7 ft. 2 in. square by 20 ft. high, two Gay-Lussac towers, and one pipe column. A continuous brimstone burner, 2½ tons daily capacity, and four pyrites kilns, each burning about 1 ton of ore daily, constitute the burner plant.

Working records are given during one winter month and one summer month, showing yields of 91·4 and 86·6% respectively, calculated on the sulphur burnt. The atmospheric temperature at 11.30 a.m. in the summer and winter is given at 29° and 26° C. respectively.

Records of the make of the chambers, as contrasted with the pipe column (4 ft. square by 14 ft. 6 in. high) were made during one week in June. The results show that although the pipe column required only 50 cub. ft. for 1 cwt. of 123° Tw. acid daily, the lead area per cwt. is much more than in the first three chambers. It is concluded that the ratio of surface to capacity is an important factor as affecting production and deserves careful attention.

Mills-Packard water-cooled sulphuric acid chambers have been installed by twenty-three different companies.[117] The first two chambers were erected in 1914 and the number of chambers of this type has increased to 112 at the present time. The war interfered with the possible development of the plant abroad, but in 1918-19 an installation of eight chambers, 18,750 cub. ft. each, was erected in New Zealand and during 1920-21 a number of chambers, 7330 cub. ft. each, including installations of 6, 8, and 12 chambers, have been erected in France and Italy.

The working of the two chambers 40 ft. high and 7330 cub. ft. each, erected for experiment, gave results corresponding to a chamber space of 3 to 4 cub. ft. per lb. of sulphur charged. Later experience and data obtained from various installations have confirmed these results and indicate the possibility of further progress in the development of this type of chamber. Mills-Packard chambers have been built in three sizes, of 7330, 11,890, and 18,750 cub. ft. each, and 40 ft., 47 ft., and 48 ft. high respectively. Plants composed entirely of the small or intermediate size chambers are actually operating at below 4 cub. ft. chamber space. (No data is available yet from the largest size chambers working.) Combined plants of the small chambers with ordinary chambers are operating at from 6 to 10 cub. ft. chamber space, and very important and satisfactory results are being obtained from the combination of a Mills-Packard chamber with another intensive system, leading to the opinion that an even lower chamber space than the

116 Austral. Inst. Min. and Met.; *Chem. Trade J.*, 1921, **68**, 133; *J.*, 1921, 145A.

117 W. G. Mills, private communication.

3 to 4 cub. ft. at present required on a Mills-Packard plant is possible.

Actual working results reported give 12 months' production of acid from a plant of six small-size chambers as 6866 tons 1 cwt. of 140 Tw. and the production of acid from a plant of six intermediate size chambers as equal to 129 tons of SO_3 per week, both from pyrites. One company burning sulphur has reported a sulphur efficiency of 95% over a period of 5 weeks and a nitrate of soda consumption of 2·2% over the same period. Other figures for nitre consumption reported have been from 2½% to 4% on sulphur burned. For the intermediate size chambers a figure of 3·62% on sulphur with a chamber space of 3·66 cub. ft. has been reported. It has been found with efficient water-cooling the wear and tear of lead has been reduced to a minimum.

It is difficult to state definitely in view of present knowledge whether the large chambers offer much advantage over the small ones from a production standpoint, but for various reasons it is likely that the larger chambers will be developed considerably in the near future.

P. Parrish and The South Metropolitan Gas Company[118] have found that the manufacture of sulphuric acid is materially promoted when sulphurous gases are brought into intimate contact with nitrous vitriol. This is best effected by using closed, lead-lined tanks, from the roof of which partitions depend, the lower edges of which terminate in a series of serrations which are immersed in nitrous acid to a depth not exceeding 4 in. The sulphurous gases enter at one end of the tank, and after bubbling under each partition escape at the other end. The plant necessitates only a minimum of power, which can be provided in the shape of one or more Kestner fans.

C. J. Reed[119] produces concentrated sulphuric acid by making provision for heating a mixture of air, sulphur dioxide, and a nitrogen oxide, absorbing the gaseous products by reaction in concentrated sulphuric acid, and then eliminating therefrom the oxide of nitrogen.

For increasing the efficiency of the manufacture of sulphuric acid by the contact process, M. Leeck[120] places one fan between the burners and the purification plant for the sulphurous gases, and a second between the contact chamber of the absorption plant. The gas composition lends itself to ready and easy control by the double provision indicated.

S. Barth[121] has patented apparatus for the concentration of

[118] E.P. 156,328; *J.*, 1921, 146A.
[119] U.S.P. 1,363,918; *J.*, 1921, 146A.
[120] G.P. 307,092; *J.*, 1921, 147A.
[121] G.P. 304,343; *J.*, 1921, 147A.

sulphuric acid, by providing throughout the whole length of the concentration vessel lateral divisions with staggered perforations over which the acid flows. The sections thus formed are connected by separate pipes with a gas exit main. Suitable provision is made for cleaning the various sections.

An interesting contribution on the subject of lead corrosion with relation to sulphuric acid manufacture, on which there is singularly little practical information available, is made by W. G. McKellar.[122] The conclusions reached suggest that wastage and destruction of lead in chamber work arise from faults inherent in the manufacture of sulphuric acid; that the rolling of lead may contribute its quota. It is suggested that analysis alone is without value in disclosing the sources of trouble in lead, but if used in conjunction with micrographic work, elucidation of the trouble may be afforded. The author declares that the advantage of a small percentage of copper with lead is largely mythical, and that observations and experiments alike point to the desirability of using Pattinsonian lead as contrasted with the lead produced by the Parkes process.

Unione Italiana fra Consumatori e Fabbricanti di Concimi e Prodotti Chimici and A. Sonneck[123] protect the construction of leaden chambers of any desired shape of great height in proportion to their horizontal cross-section, the gas connexion between adjacent chambers being at a low level.

An interesting history of the manufacture of sulphuric acid in the Dominion of Canada is given.[124]

The Badische Anilin u. Soda Fabrik[125] patent a tubular heated chamber for the concentration of sulphuric acid in vacuum. The pipes are of perforated sheet iron, homogeneously coated internally and externally with lead. These pipes resist the chemical action of the boiling liquid, and also the difference of pressure. The chamber is lead-lined and the pressure is a continuous one.

Provision is made by J. H. Brown[126] in the manufacture of sulphuric acid for a method of washing burner gases and the reheating of such washed gases prior to oxidation.

G. Gianoli[127] discusses the advantages and disadvantages attending the different methods proposed for supplying nitrogen oxides in the manufacture of sulphuric acid, particularly as affecting his own proposed method of employing in the Glover tower a mixture of sulphuric and nitric acids by introducing sulphuric acid of sp. gr. 1·16 along with a concentrated solution of sodium nitrate, and of removing the sodium bisulphate which crystallises out on cooling.

[122] J., 1921, 137T.

[123] E.P. 164,627; *J.*, 1921, 543A.

[124] *J.*, 1921, 231R.

[125] G.P. 302,553; *J.*, 1921, 388A.

[126] U.S.P. 1,365,964; *J.*, 1921, 178A.

[127] *Giorn. Chim. Ind. Appl.*, 1921, 3, 11; *J.*, 1921, 213A.

An interesting article having reference to the Gaillard sulphuric acid concentrating tower and the electrical precipitation of acid is contributed by M. Kaltenbach.[128] After dealing with one of the theoretical principles of concentration and describing certain experiments to show that a true static equilibrium is approached, which implies that concentration of the liquid acid in equilibrium with the vapour varies almost directly with the temperature, the author concludes that no process can alike give strong condensed acid and complete condensation. It is stated therefore that the function of the Cottrell process is limited to the aggregation of the vesicular acid formed at the moment of condensation. The author rightly suggests the use of two small coke scrubbers, each preceded by an efficient cooling coil. The first condensate should be of a minimum strength to admit of economical concentration, the second condensate being discarded.

That the manufacture of sulphuric acid in Germany[129] is intimately bound up with the zinc industry is demonstrated by the fact that in 1913 Upper Silesia produced 255,589 tons of acid of 50° B., or 9·7% of the total German production, and also 3137 tons of anhydrous liquid SO_2. In 1919 and 1920 the outputs were 52,887 tons and 87,960 tons respectively.

T. Lewis Bailey[130] refers to the good results, both as regards nitre-consumption and exit-acidity, obtained in a new plant, of which the chambers were all of the Mills-Packard conical, externally water-cooled type. By reason of the economy in ground space and materials of construction, it is suggested that greater importance is being attached to intensive work. This necessitates closer supervision and the necessity for efficient scientific control is urged. It is predicted that an increasing amount of high-strength acid will be made by the contact process. Reference is made to an unsuccessful attempt made to absorb the nitrous gases in a sulphuric acid plant by mechanical means instead of in a Gay-Lussac tower. It is suggested that it would appear necessary to improve the atomisation of the acid and to augment the time of contact.

R. E. Dior[131] protects the construction of sulphuric acid chambers formed of two frusto-conical portions, the sides of the lower portion being more inclined to the vertical than those of the upper, and the whole chamber thus having approximately the shape of an inverted funnel. An inlet pipe near the bottom and an outlet pipe near the top are arranged tangentially to the chamber walls so as to promote spiral circulation of the gas against the walls, which are cooled externally by a flow of water.

[128] *Chim. et Ind.*, 1921, 5, 143; *J.*, 1921, 256A.
[129] *J.*, 1921, 257R.
[130] *J.*, 1921, 279R.
[131] E.P. 164,572; *J.*, 1921, 582A.

A process for the manufacture of sulphuric acid and hydraulic cement is covered by Farbenfabr. vorm. F. Bayer u. Co.[132]

T. A. Clayton[133] protects a sulphur-burning furnace in which the air is projected downwards through one set of jets on to the burning sulphur, whilst the remainder is directed upwards, through the other set, so as to promote mixing of the gas produced and oxidise any volatilised sulphur.

T. Schmiedel and H. Klencke[134] protect a process for the production of sulphuric acid, in which the essential principle is to bring the gases, after serving to denitrate the usual quantity of acid, into contact with excess nitrosylsulphuric acid, in one or more pairs of small chambers where special provision is made to ensure intimacy of contact.

A. M. Fairlie[135] in a series of articles deals with recent developments in the sulphuric acid industry.

Dust Precipitation.—It is stated that mechanical methods of dust precipitation have largely given place to electrical methods. A modification of the Cottrell treater has been developed in which sheet iron screens having diamond or square meshes are placed in parallel and transversely to the gas flow. These screens are grounded electrodes, and charged electrodes, in the form of wires, are suspended vertically between the screens.

This form of treater appears effective for lead smelting gases, having a temperature of 400° F., but nothing can yet be said concerning sulphur furnace gases of about 800°–1000° F.

Nitration.—Fairlie remarks that there has been a tendency to instal nitre pots outside the flue and fire them with coal. Extra expense is said to be more than balanced by their efficiency when restarting a plant, and by the avoidance of nitre cake in burner flues. In some plants nitre solution is sprayed into the first chamber. This, of course, results in the formation of sodium nitrate in the acid. Close inspection of the atomising nozzles is necessary, otherwise streams of nitre solution may fall into the chamber with the formation of nitric acid and consequent corrosion of the lead work.

Little progress has been made with ammonia oxidation plants.

Tower and Chamber Construction.—Towers of acid-proof masonry without lead side sheets are a recent development. The towers are supported by steel angles held together by tie-rods, and are lined with acid-proof tiles. The Glover tower is packed with bricks, while manufactured forms of packing are preferred for the Gay-Lussac towers. Inter-chamber or cooling towers have been installed

[132] G.P. 297,922 and 299,033; *J.*, 1921, 582A.

[133] E.P. 166,961; *J.*, 1921, 657A.

[134] G.P. 149,648; *J.*, 1921, 693A.

[135] *Chem. and Met. Eng.*, 1921, 25, 861, 917, 964, 1005.

at many works, the purpose of these being to supplement large chambers in the matter of heat dissipation, and to produce a lower temperature of the gas mixture.

Steam, as a means of hydration, has been superseded almost entirely by water, and various types of atomising nozzles have been designed.

Acid Circulation.—Several attempts have been made to develop a satisfactory mechanical acid pump. Rotary pumps of antimonial lead and silicon-iron are largely used, and these are for the most part direct electrically-driven. The Lewis pump, originally of the vertical submerged type, has been successfully developed into an outside vertically-driven rotary pump.

Processes.—Two processes for the manufacture of sulphuric acid, without chambers, have been proposed. The "pipe" process of Kaltenbach utilises a number of tubes packed inside and water-jacketed. Gases leaving the Glover tower are passed through the tubes in counter-current to the acid, which is mixed as required with water. Among the advantages claimed for the process are: (1) Ease of controlling temperature; (2) effective heat interchange; (3) independence of atmospheric conditions; (4) elimination of water sprays.

The packed cell process is similar to the Opl plant.

Silica Gel.—The method of manufacturing silica gel and apparatus in which it is used for the separation of gases and vapours, has been patented. It is stated that from a gas mixture containing 8·75% SO_2, the gel will absorb 6·8% of its weight of SO_3, and it has been proposed to use this property for effecting economies in plant and manufacture of sulphuric acid. The conversion of SO_2 to SO_3 catalytically by passing the gas through the gel containing a catalysing agent is still in the experimental stage.

SULPHUR.

A patent by H. C. Pedersen[136] has reference to the extraction of sulphur from sulphide ores. By regulating the ore supply at the bottom of the shaft furnace in which iron pyrites or other sulphide ore is roasted along with a quantity of coke insufficient for the reduction of the ore to metal, sulphur vapour distils off, and can be suitably collected.

N. E. Rambush[137] removes sulphur from hydrogen sulphide gases by washing the latter with a suspension of ferric hydroxide in ferrous sulphate solution. A current of air is made to ascend a tower against the flow of the suspension. The sulphur is separated by fractional subsidence or by centrifuging a portion of the revivified suspension.

[136] E.P. 152,887; *J.*, 1920, 819A.
[137] E.P. 153,665; *J.*, 1921, 9A.

The separation and recovery of sulphur from solutions, gases, and vapours containing hydrogen sulphide is effected by passing the gases mixed with oxygen over a solid contact mass suitably prepared.[138] The oxides and hydroxides of iron, manganese, aluminium, and allied metals, or mixtures of these, are suitable for use in this connexion. The polysulphides which are formed can be decomposed into sulphur and hydrogen sulphide, and the latter gas again returned to the process for conversion into sulphur.

Sulphur recovored by the carbon bisulphide extraction process from spent oxide is invariably dark or black in character owing to the presence of hydrocarbons which accompany the extracted sulphur. Attempts have been made from time to time to purify the sulphur thus extracted so as to render it at least equal to Sicilian sulphur. Fractional crystallisation has been resorted to with fairly satisfactory results.

J. J. Hood[139] treats a solution of sulphur in carbon bisulphide such as is obtained from spent oxide by agitation with 1–2% by volume of sulphuric acid (sp. gr. 1·8) and effects in this way the removal of a considerable quantity of tarry matter. Either before or after filtration the mixture is agitated with 5–10% by volume of water and the aqueous layer containing the impurities is removed. Finally, the sulphur solution is made to percolate through alumina or bauxite, the carbon bisulphide evaporated, and pure sulphur remains as a residue.

N. E. Katz and H. M. Little's[140] apparatus for and method of separating sulphur from sulphur ores comprise the use of an autoclave, in which the ore is heated with water until the sulphur is melted by the steam generated.

The treatment of mined sulphur is covered by R. F. Bacon and H. S. Davies.[141] To improve the free-burning quality of such sulphur containing oil, heating to 400°–430° C. for a special time to carbonise the oil is recommended. The product may be allowed to cool to a temperature above the melting point of sulphur and stand until the carbon is separated.

Although the year 1920 was marked by considerable increases in production and exportation of Sicilian sulphur, production rising from 181,744 to 240,857 metric tons, and exports increasing from 147,286 tons to 188,865 tons, the figures compare badly with those for 1914, when 340,700 tons was exported and stocks amounted to 359,800 tons. Exportation has been affected by the fluctuating exchange.[142]

[138] Gewerkschaft des Steinkohlenbergwerks Lothringen and G. Wiegand; G.P. 326,159; *J.*, 1921, 9A.

[139] E.P. 155,692; *J.*, 1921, 115A.

[140] U.S.P. 1,365,922; *J.*, 1921, 148A.

[141] U.S.P. 1,374,897-8; *J.*, 1921, 433A.

[142] *Chem. Ind.*, 25. 4. 1921; *J.*, 1921, 219R.

K. P. McElroy[143] patents a method of making carbon bisulphide. Fuel and sulphur are charged into a shaft similar to a gas-producer with an air inlet at the base. Carbon bisulphide is recovered by scrubbing with oil the gases thus generated.

L. H. Diehl[144] treats of the recovery of sulphur from blast-furnace slags.

Thorium Compounds.

H. Wade[145] prepares, by dissolving 120 g. of thorium sulphate, $Th(SO_4)_2,8H_2O$, in 50 c.c. of 80% phosphoric acid and heating for 10 hours at 280° C., white acicular crystals of a double metaphosphate and sulphate of thorium, $Th(PO_3)_2SO_4$. This compound is said to be purer than the compound prepared by a method previously indicated.[146]

Monazite sand is treated with concentrated sulphuric acid, and after the removal of soluble impurities, the insoluble thorium compound is converted to thorium hydroxide.[147]

Zinc.

The Metallbank u. Metallurgische Ges. A.-G.[148] protect a process for treating sal-ammoniac skimmings, suitably pulverised, with the necessary dry slacked lime, moistened with 15% of its weight of water, and treated with live steam. The ammonia evolved is recovered and the residue is leached with water, yielding zinc oxide and a solution of calcium chloride.

Zinc Oxide.

In the manufacture of French zinc oxide J. A. Singmaster[149] provides for the contents of the retorts, in which the zinc is volatilised, being kept nearly constant by the addition from time to time of molten zinc.

Zirconium.

J. G. Thompson[150] deals with the electric furnace purification of zirkite (impure zirconia), feeding into an arc furnace a mixture of zirkite with sufficient coke to transform the silica only to silicon carbide; 90–95% of the silica may be volatilised as carbide. With greater amounts of coke the elimination of the silicon is less complete. Zirconium carbide may be converted into oxide by ignition in air by a dull red heat.

143 U.S.P. 1,369,825; *J.*, 1921, 300A.
144 *Stahl u. Eisen*, 1921, 41, 845; *J.*, 1921, 506A.
145 E.P. 156,892; *J.*, 1921, 178A.
146 U.S.P. 1,323,735; *J.*, 1920, 517A.
147 H. N. McCoy, U.S.P. 1,366,128; *J.*, 1921, 178A.
148 E.P. 145,085; *J.*, 1921, 734A.
149 U.S.P. 1,372,462; *J.*, 1921, 346A.
150 *Trans. Amer. Electrochem. Soc.*, 1921, 291; *J.*, 1921, 768A.

GLASS.

By W. E. S. Turner, D.Sc., M.Sc.,

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Just before completing this report a copy of the *Sprechsaal Kalender* for 1922 came to hand. This publication is fairly well known, certainly on the Continent, and it was interesting to peruse its data. There were but half a dozen or so references to investigations in glass technology and ceramics since 1914, and one wonders whether it is due to the comparative poverty of German research on these subjects over this period, or to the habit displayed so frequently in German scientific circles of neglecting in a large measure scientific work not made in Germany. Certainly, however, data in quite a number of portions require overhauling in the light of the numerous researches in the last few years, both in this country and in America. As to glass research in Germany, the technical journals of that country for the past year have made very poor reading.

A review of the scientific investigations in glass technology during 1921 does reveal this country in a very good light. It is rather striking that American activity has fallen off very greatly, if one is to judge by published investigations. In Great Britain, however, research shows little or no sign of slackening and the output of work has been maintained certainly at the level of the preceding year. We may hope that it is a good augury for the industry of the future.

Of the organised research efforts, reference may be made to three matters of interest. The first is the big extension of the Department of Glass Technology in the University at Sheffield, which has now entered into extensive premises formerly used as a glass works with two glasshouses. Here are adequate facilities at least for all kinds of operations in glass technology. Further, the Glass Research Association has got into working stride, and although open publication of its work has not, as yet, occurred, it is known to be making very good progress. Finally, in this connexion certain recent developments in the American Ceramic Society will be watched with considerable interest. A full-time organising secretary has been appointed, amongst whose duties it will be to visit members, especially the corporation members, and investigators, and help to stimulate research.

It is needless to remark that the glass industry in this country has felt very acutely the trade depression of 1921. As an industry it prospered with others during the war. Prior to the war, however, as a whole, it was comparatively poor and possessed but few reserves to stave off hard times such as the present. The matter is of interest, however, especially from the fact that, faced with a period of depression, quite a number of manufacturers have still gone forward with their extensions and revolutionary changes in the works. Modern plant and machinery have been installed in quite a number of works during the period under review. A good deal of the machinery, it is true, is American, for although the ordinary lines of research do not appear to have produced very fruitful results in America during 1921, inventors in that country still show ceaseless activity in regard to machines and general labour-saving devices. Not only are these items of equipment being installed in this country in many works, but the writer's experience has been that manufacturers were never so ready to appeal for scientific assistance for the improvement of their goods as at the present time. The outlook, therefore, is not without hope.

The Melting and Working of Glass

The oft-discussed subject of the influence of alumina on the melting, working, and other properties of glass has been carried to a more definite stage as the result of a series of papers from the Department of Glass Technology, University of Sheffield. V. Dimbleby, F. W. Hodkin, and W. E. S. Turner[1] show that in a series of trisilicate glasses of general composition $xNa_2O,yAl_2O_3,6SiO_2$, where $x+y=2$, the maximum amount of alumina capable of being introduced and worked up to temperatures 1400°–1425° C. is about 12·7%. A moderately hard lime glass (6 SiO_2, 1·1 Na_2O, 0·9 CaO) is also made more fusible when 0·1 mol. of CaO is replaced by 0·1 mol. of Al_2O_3. Alumina was shown to prevent devitrification.

F. W. Hodkin and W. E. S. Turner[2] have shown that with a soda-lime glass containing about 8% of CaO, such as is used with automatic bottle machines, the batch melts most rapidly and is most fluid when the source of alkali is present as soda ash and the lime as burnt lime. With soda ash slaked lime is better than limespar or limestone. The batches containing sand, salt cake, and either burnt or slaked lime were the slowest in melting and most viscous in working. Several other mixtures were tested.

A matter not of general knowledge, namely, the commercial substitution of glass containing lead for electric light bulbs by an alkali-lime-magnesia glass,[3] has become better known by the

[1] *J. Soc. Glass Tech.*, 1921, **5**, 107 ; *J.*, 1921, 509A.

[2] *Ibid.*, 1921, **5**, 188 ; *J.*, 1921, 770A

[3] Corning Glass Co., E.P. 145,428 ; *J.*, 1921, 82A.

publication of the patent specification covering the new type of glass.

The melting properties of the soda-lime-magnesia trisilicate glasses have also been investigated by V. Dimbleby, F. W. Hodkin, and W. E. S. Turner,[4] and it is found that in comparison with the glass $6SiO_2$, $0{\cdot}8CaO$, $1{\cdot}2Na_2O$ on the one hand, and $6SiO_2$, $0{\cdot}8$ MgO, $1{\cdot}2$ Na_2O on the other, glasses over the range up 0·5 CaO, 0·3 MgO are more easily melted than any of the others, whilst all the glasses containing both oxides are more readily annealed and are softer than those at the extremes of the series.

The manufacture of heat-resisting glass from a batch containing sand 1300 lb., soda ash 400 lb., lime 200 lb., borax 20 lb., nitre 40 lb., artificial biotite 40 lb., manganese dioxide 85 grams, titanium oxide 30 g., nickel oxide 35 g. has been described by G. Alleman.[5] Such glass, in the form of polished plate ¼ in. thick, absorbs 78% of the incident heat rays, transmits 42% of ordinary light and has considerable mechanical strength. E. W. Tillotson[6] has also given a general account of the present position of the manufacture of constructional glass. Fire-resisting glass still continues to receive the consideration of inventors and a further specification by V. Shuman [7] may be noted.

Several papers or specifications have appeared dealing with processes necessary to produce glass free from seed and striæ. Thus, F. E. Wright[8] gives charts showing the allowance to be made for the volatilisation of lead oxide, boric oxide, and the alkalis during the manufacture of optical glass. The same author in another paper[9] describes a method of distinguishing between surface markings and cords in glass by immersion in a liquid of the same refractive index as the glass. In such circumstances the surface markings disappear and the cords are clearly defined. The fining of glass is the subject of two patent specifications,[10] the one by Schott u. Gen., in which high pressure is applied to the molten glass, the other by W. G. Clarke and L. N. Bruner using an electric current.

In connexion also with the subject of the fining and other phenomena in glass, a paper of first-class importance by E. W. Washburn, E. F. Footitt, and E. N. Bunting[11] describes apparatus for the determination of the gases remaining dissolved in plain optical glass. The gases extracted were oxygen, nitrogen, and carbon

[4] *J. Soc. Glass Tech.*, 1921, **5**, 352.
[5] *J.*, 1921, 241T.
[6] *J.*, 1921, 155T.
[7] U.S.P. 1,355,625.
[8] *J. Amer. Ceram. Soc.*, 1920, **3**, 783 ; *J.*, 1921, 10A.
[9] *Ibid.*, 1921, **4**, 655 ; *J.*, 1921, 890A.
[10] E.P. 147,487 ; *J.*, 1920, 750A. E.P. 161,192.
[11] *Univ. of Illinois Bulletin*, 1921, **18**, No. 15 ; *J.*, 1921, 433A.

dioxide, the total percentage by weight varying from 0·01 for a borosilicate to 0·043 for a barium flint glass.

S. R. Scholes, L. W. Nicols, and W. F. Kaufman[12] propose a novel method for the elimination of striæ and the substitution of the ordinary stirring method. The process consists in mounting the pot at a slight angle in the furnace on a rotatable bed.

An interesting paper, illustrative of the efforts made to produce during the war optical glass at a third British factory, is that by J. W. French,[13] who describes the general process of manufacture adopted.

Reference may also be made to the analytical work of M. Ikawa,[14] on the amount of sodium sulphate, chloride, and carbonate in window glass. Of the first-named, 0·667–1·04% was found in various commercial samples, and the results may certainly be used to illustrate the fact of incomplete reactions in glass making.

In connexion with the after-working or decoration of glass, reference may be made to papers by O. Schwarzbach,[15] who describes in detail the conditions for the production of iridescence and lustre on glass pearls and beads, and by C. Fleck,[16] who deals with the chromate-albumin copying process. J. Rheinberg[17] patents a process for producing metallic coatings on glass by means of collodion containing a salt of the metal and heating to 600°–750° C. after application.

Special attention must be directed to the valuable series of papers and discussions on the silvering of glass embodied in a joint publication of the Physical and Optical Societies.[18] The papers not only deal with several of the old standard methods but also contain very useful suggestions resulting from practical experience.

The devitrification of series of alkali-lime, alkali-lead oxide, and alkali-barium oxide glasses under conditions such as might be expected to occur during optical glass manufacture has been studied by C. J. Peddle,[19] who found the lime glasses more prone to devitrification than the lead oxide ones, especially when the alkali was soda. Lead oxide glasses almost always deposit silica on devitrification and lead silicate separation is only likely to occur when the PbO content of the glass exceeds 70%. In regard to the barium oxide glasses, silica was more readily deposited from soda glasses than from the potash ones, whilst barium silicate more

[12] U.S.P. 1,370,673; *J.*, 1921, 303A.

[13] *Optician*, 1920, **59**, 335, 351; **60**, 3, 18, 28.

[14] *J. Chem. Soc. Japan*, 1921, **42**, 768; *J.*, 1921, 847A.

[15] *Sprechsaal*, 1921, **54**, 369.

[16] *Ibid.*, 1921, **54**, 340.

[17] E.P. 156,472; *J.*, 1921, 149A.

[18] Discussion on "The Making of Reflecting Surfaces," published by the Physical Society and Optical Society, Nov., 1920.

[19] *J. Soc. Glass Tech.*, 1921, **5**, 72, 256; *J.*, 1921, 509A, 890A.

easily separated from the potash than from the soda glasses. Photomicrographs of the various types of crystalline deposit accompany the papers.

These same papers of Peddle also recorded the relative effects of lime, lead oxide, and barium oxide on the durability of glass, the test being based not only on the solubility in water of glass powder, but also on exposure to the atmosphere. When glasses of corresponding molecular composition are compared, those containing lime are more durable than those with lead oxide, unless the alkali content falls below 15%. Weight for weight, it is found that up to a percentage content of CaO or PbO of 20%, the lime glasses weather better than those from lead oxide. A result of very great interest and importance is the discovery that a glass containing both soda and potash is more durable than a glass with an equivalent percentage of either oxide alone. This had also been indicated in an investigation by Hodkin and Turner,[20] and C. J. Peddle[21] has now carried the matter considerably further by showing that in the four series 60% SiO_2, 30% PbO, 10% (Na_2O+K_2O); 50% SiO_2, 40% PbO, 10% (Na_2O+K_2O); 60% SiO_2, 20% PbO, 20% (Na_2O+K_2O); and 50% SiO_2, 30% PbO, 20% (Na_2O+K_2O), a minimum solubility is reached at the point where the ratio of the percentage of potash to soda is 7 : 3.

Reference must also be made to some very interesting experiments by C. J. Peddle [22] on iridescent and other effects on the surfaces of lead oxide and barium oxide glasses due to the action of carbon dioxide, hydrogen, sulphide, sulphur dioxide, and hydrogen chloride. In the absence of moisture no action was found after three months. When wet, the thickest layers of deposit, indicating most marked action, were obtained with carbon dioxide and hydrogen sulphide on lead glasses and sulphur dioxide and hydrogen chloride on the barium glasses.

The Physical Properties of Glass.

Density.—An important paper by W. L. Baillie [23] involves the recalculation from existing data of the density factors previously given by Winkelmann. The new factors, namely, SiO_2 2·24, Al_2O_3 2·75, Sb_2O_3 3·0, B_2O_3 2·90, As_2O_3 3·33, ZnO 5·94, BaO 5·00, CaO 3·30, MgO 3·60, PbO 9·30, K_2O 2·66, and Na_2O 2·55, make it possible to calculate densities much more closely in agreement with experiment than by the Winkelmann factors. S. English and W. E. S. Turner,[24] based on their measurements of the density

[20] *Ibid.*, 1920, **4**, 120; *J.*, 1920, 546A.
[21] *Ibid.*, 1921, **5**, 195; *J.*, 1921, 771A.
[22] *Ibid.*, 1921, **5**, 265; *J.*, 1921, 890A.
[23] *J.*, 1921, 141T.
[24] *J. Soc. Glass Tech.*, 1921, **5**, 277; *J.*, 1921, 890A.

of sodium aluminium trisilicate glasses, suggest that Baillie's factor for Al_2O_3 is still of doubtful accuracy.

Annealing Temperature.—This subject still attracts attention. It is suggested by L. H. Adams and E. D. Williamson [25] that optical glass should be annealed at a comparatively low temperature so that recurrence of strain on cooling is practically eliminated. They propose also that glass should be considered annealed when the optical path difference along the middle of a slab of glass between the ordinary and extraordinary rays does not exceed 5 $\mu\mu$ per cm.; whilst the annealing temperature is defined as that value at which the path difference is reduced from 50 to 5 $\mu\mu$ per cm. in a definite time interval. F. Weidert and G. Berndt[26] adopt the method of measuring the difference of refractive index between the two rays before and after cooling from various temperatures between 600° and 200° C. and plotting the difference against the temperature before cooling. The required annealing temperature is indicated by a sharp bend in the curve. For flint glasses the deformation temperature is 40°–50° C. higher; for crown and flint glasses 70°–100° C. Of other methods for determining stress in glass one may refer to the further study of that of Coker, by A. L. Kimball.[27]

Further studies on the relation between chemical composition and upper annealing temperature have been published in two papers by S. English and W. E. S. Turner, the one relating to the effect of alumina,[28] the other mixed lime-magnesia glasses.[29] The glasses of the 6 SiO_2, xAl_2O_3, yNa_2O series, where $x+y=2$, have, generally speaking, lower annealing temperatures than similar glasses containing either lime or magnesia. Glasses containing varying proportions of lime and magnesia and lying intermediate between $6SiO_2,0{\cdot}8CaO,1{\cdot}2Na_2O$ and $6SiO_2,0{\cdot}8MgO,1{\cdot}2Na_2O$ have considerably lower annealing temperatures than for these extremes, a result not only of interest but of considerable practical importance.

Viscosity.—This is related to the annealing temperature and other properties, and its connexion with composition has been studied by E. W. Washburn and G. R. Shelton.[30] It is shown that a medium flint and light barium crown glasses were least viscous of the seven different glasses tested, whilst the light flint was most viscous. In regard to methods of determination, I. Masson, L. F. Gilbert, and H. Buckley [31] have developed one based on the rate of fall of a metal sphere in a viscous fluid. In a furnace the progress of the experiment is followed by means of X-ray photographs.

[25] *J. Opt. Soc. Amer.*, 1920, **4**, 213; *cf. J.*, 1921, 81A.
[26] *Z. tech. Phys.*, 1920, **1**, 51; *J.*, 1921, 46A.
[27] *J. Opt. Soc. Amer.*, 1921, **5**, 279.
[28] *J. Soc. Glass Tech.*, 1921, **5**, 115; *J.*, 1921, 509A.
[29] *Ibid.*, 1921, **5**, 357.
[30] *Phys. Rev.*, 1920, **15**, 149.
[31] *J. Soc. Glass Tech.*, 1921, **5**, 337.

Thermal Expansion.—Further additions to our knowledge of the influence of composition have been made. In a study of the effect of silica and of sodium oxide, it is shown by S. English and W. E. S. Turner [32] that sodium oxide has the same influence on the expansion of glass whether a second base such as lime is present or absent. Evidence is also obtained that fused silica carries into glasses its own rate of expansion. The effect of alumina introduced in molecular quantities into the trisilicate glasses is shown by the same authors [33] to reduce thermal expansion as compared with lime or magnesia. A third paper by English and Turner [34] on mixed lime and magnesia glasses shows that the thermal expansion does not appear to undergo any abnormal change on mixing the bases.

The abnormal rate of expansion and the heat absorption in the neighbourhood of the softening temperature have received further consideration. W. B. Pietenpol[35] differs from Peters and Cragoe in finding, just beyond the region of rapid expansion, not a contraction but only a decrease in the coefficient of expansion. A. Q. Tool and C. G. Eichlin [36] show that heat treatment and powdering both influence the range of temperature over which abnormal heat absorption is found as also the tendency of the glass to crystallisation.

A simple test is described by D. E. Sharp [37] for ascertaining the relative thermal expansions of two glasses which are to be welded. The method consists simply in drawing out a compound strip or riband which will remain straight or will curl according as the expansions are equal or dissimilar. F. E. Wright [38] proposes a further but less simple test.

Optical Properties.—The most important studies of the year as regards the relation between composition and optical properties are again those of C. J. Peddle. In a series of six papers,[39] this author makes a comparison of the alkali-lime-silica and the alkali-lead oxide-silica glasses, and describes numerous experimental results showing the relative effects on refractive index, dispersion and other properties, in glasses containing silica, sodium and potassium oxides, and barium oxide. A comparison is also made between the lead oxide and the barium oxide glasses. It is shown that when compared by molecular composition, the lead oxide glasses have a higher value of n_D than the lime glasses, whilst when comparison is made by percentage composition it is the lime glasses

[32] *Ibid.*, 1921, **5**, 121; *J.*, 1921, 510A.
[33] *Ibid.*, 1921, **5**, 183; *J.*, 1921, 771A.
[34] *Ibid.*, 1921, **5**, 358.
[35] *Glass Industry*, 1921, **2**, 162.
[36] *J. Opt. Soc. Amer.*, 1920, **4**, 340; *J.*, 1921, 347A.
[37] *J. Amer. Ceram. Soc.*, 1921, **4**, 219; *J.*, 1921, 259A.
[38] *J. Opt. Soc. Amer.*, 1921, **5**, 453; *J.*, 1921, 847A.
[39] *J. Soc. Glass Tech.*, 1921, **5**, 72, 201, 212, 220, 228, 256; *J.*, 1921, 509A, 888A, 889A, 890A.

in which n_D is greater, except where the silica is less than 60% and the alkali greater than 20%. By both methods of comparison, lead oxide glasses are found to have a higher total dispersion than those made from lime. The detailed results in this set of papers are so numerous as to be beyond summary for a report of this nature.

J. R. Clarke and W. E. S. Turner[40] find that in the soda-alumina-trisilicate glasses the refractive index and dispersion decrease very slowly as alumina substitutes soda. Between $6SiO_2,0{\cdot}1\,Al_2O_3,1{\cdot}9\,Na_2O$ and $6\,SiO_2,0{\cdot}4\,Al_2O_3,1{\cdot}6\,Na_2O$, the value of υ rises from 57·4 to 60·2.

Lord Rayleigh[41] has made the interesting observation that ordinary silica glass is weakly doubly refracting, suggesting a crystalline structure.

R. J. Montgomery[42] also returns to the subject of optical properties and composition and discusses, by reference to known commercial glasses, the influence of the total RO content, and of the PbO proportion of this content, in producing alterations of refractive index. In another paper,[43] the same author discusses the various commercial types of barium oxide glasses and contrasts the influence of three pairs of oxides, namely, BaO and other RO bases, B_2O_3 and SiO_2, and B_2O_3 and Al_2O_3 on the refractive index and dispersion. Zinc oxide, in amounts up to 11%, was found to exercise but little effect on the optical properties of the glasses studied.

Glass Furnaces.

Economic pressure has directed considerable attention to improving the efficiency of glass furnaces. M. W. Travers[44] has incurred the gratitude of the glass industry by his study of the efficiency of a glass tank furnace heated by a steam-blown gas producer. He advocates as short a lead as possible from the gas producer to the furnace, not only because of the fall in temperature of the gas and the consequent loss of heat but also because of the deposition of tar, a valuable heating constituent. In regard to the regenerators, he calculates that that for the gas need not have more than half the volume of the air regenerator. The efficiencies of three tank furnaces working under different conditions, with regenerators running at 600°, 800°, and 1000° C., are compared. The energy utilised in actual glass melting runs 9, 12, and 14·5% respectively, and it is pointed out that the heat loss from the walls is the ultimate factor determining relationship between fuel consumption and glass output.

[40] *Ibid.*, 1921, **5**, 119; *J.*, 1921, 510A.
[41] *Proc. Roy. Soc.*, 1920, **A98**, 284; *J.*, 1921, 116A.
[42] *J. Amer. Ceram. Soc.*, 1920, **3**, 900; *J.*, 1921, 46A.
[43] *Ibid.*, 1921, **4**, 536; *J.*, 1921, 847A.
[44] *J. Soc. Glass Tech.*, 1921, **5**, 166; *J.*, 1921, 770A.

Four other papers discuss the same subject of glass-melting furnaces. F. J. Denk[45] deals with design and operation. An unsigned article in *Sprechsaal*[46] refers particularly to pot furnaces and discusses the volume to be allowed in the actual melting chamber. This author would allow 1 cubic metre of regenerator space in each regenerator for each $4\frac{1}{2}$ cubic metres of space in the furnace. C. de la Condamine and P. Appell[47] discuss the general question of the heat balance in furnaces. In a study of a producer gas-fired recuperative furnace, it was found that the total of heat either used in work or lost by radiation amounted to 30·7% of the energy of the coal, 13·7% being lost in recuperation, 28·9% in the exit gases, and 26·7% in the generation of the gas. Another study of heat losses from a gas-fired regenerative furnace is that of Klaften[48] who found that for each 100 calories of heat supplied to the furnace, 95·5 came from the producer and 4·5 from the steam. The useful heat absorbed in melting the glass was 12·5 calories, although 12 were recovered from the waste gases. The heat losses were 15 calories in the producer, 4 in the flues, 0·5 during reversal, 6 in the regenerators, 20 by conduction and radiation from the substructure, 23 from the superstructure, and 7 in chimney waste gases.

Reference may also be made to the proposals of A. Ferguson[49] as attempts to get away from the orthodox melting furnace and obtain greater heat efficiency by passing the batch in the form of a spray through a small conical chamber maintained at very high temperature.

Annealing furnaces have also come in for considerable attention, especially muffle lehrs. R. L. Frink[50] has introduced a new kind of muffle in the combustion chamber made of corrugated iron, preferably of high silica and low carbon content. The remainder of the lehr is also of unusual construction, being of iron framework lagged with asbestos according to the degree of cooling-off desired. W. O. Amsler[51] patents a muffle lehr in which the products of combustion are drawn round the muffle in a tortuous path and the air for combustion drawn along a second series of tortuous channels. The muffle principle in kiln annealing is already well known. M. A. Smith[52] patents an arrangement in which combustion takes place in a checker work chamber below the muffle.

[45] *J. Amer. Ceram. Soc.*, 1921, **4**, 224 ; *J.*, 1921, 259A.
[46] *Sprechsaal*, 1920, **53**, 7, 66.
[47] *Chaleur et Industrie*, 1921, Nos. 4, 5, 6 and 7.
[48] *Sprechsaal*, 1921, **54**, 251.
[49] E.P. 154,251 ; *J.*, 1921, 46A.
[50] E.P. 169,537 ; *J.*, 1921, 813A.
[51] U.S.P. 1,341,031 and 1,351,323 ; *see also* U.S.P. 1,385,868 ; *J.*, 1921, 658A.
[52] U.S.P. 1,342,233 ; *J.*, 1920, 519A.

Annealing furnaces for special operations have been designed by D. E. Sharp[53] and by W. A. Whatmough.[54] The former gives working drawings for an annealing furnace for optical glass whilst the latter describes a gas-heated furnace for the re-annealing of lampworked and other light glass articles and demonstrates how successfully annealing can be done if carried out on the previously determined annealing points of the glass.

E. F. Collins[55] describes the construction of electrically-heated lehrs suitable for high-grade glassware. He prefers the vertical form as being more efficient than the horizontal and claims to have effected a saving over the ordinary annealing processes.

Glass Machinery and Glass Making Processes.

Practically all the advances made in this branch of glass technology are subject to patents. They are very numerous and it is not possible to do more than mention outstanding developments Great interest is centred in methods of delivering glass automatically to machines, blowing bulbs, and blowing and pressing heavy glassware and bottles, and drawing sheet glass and cylinder glass. The improvements proposed in the last-named case are almost all questions of details and will not be referred to.

In connexion with the feeding of glass to machines, the historical development of the subject is dealt with very ably in a paper by G. Dowse and E. Meigh[56] and the various devices up to most recent times are described in a manner enabling the reader to get a grip of the subject.

Where machines are fed by hand-gathering, the charging of the glass into the parison mould on bottle machines is not always carried out precisely. K. E. Peiler[57] describes a device for remedying this defect and for shaping the charges by means of a funnel the inner surface of which is continuously lubricated by a special arrangement. A. R. Hunter[58] also suggests a method of preventing too hard a skin from forming on the parison by removing the latter very slightly out of contact with the mould after formation.

Of the numerous specifications in connexion with glass feeding devices, those in connexion with the Hartford-Fairmont feeder occur most frequently. K. E. Peiler[59] has worked out an arrangement for shaping the charges of glass to fit the mould, the cross-section of the glass at various points being controlled by varying

[53] *J. Amer. Ceram. Soc.*, 1921, **4**, 597.

[54] *J. Soc. Glass Tech.*, 1921, **5**, 44 ; *J.*, 1921, 510A.

[55] *J. Amer. Ceram. Soc.*, 1921, **4**, 335 ; *J.*, 1921, 510A.

[56] *J. Soc. Glass Tech.*, 1921, **5**, 134.

[57] E.P. 157,160.

[58] E.P. 142,929.

[59] E.P. 142,785 and 142,786.

the rate of discharge from the orifice, a reciprocating plunger or impeller being employed for this purpose to act on the charge. The British Hartford Fairmont Co. and J. O. Burge[60] also patent a device for varying the weight of the charge.

Novel methods mark several of the recent feeding devices. E. H. Langwell[61] has devised an arrangement in which the molten glass flows through a channel in the tank furnace wall into one of a series of rotating nozzles directed at right-angles, that is, vertically downwards, from the channel. S. D. Olsen[62] proposes to permit the charge of glass, after being severed by shears, to drop into a small trough, immediately below where it takes the form of a strip and is then ejected, by tilting the trough, into the parison mould; R. T. McGee[63] has devised a system in which glass flows into passages and a chamber constituting an arrangement like a pump. By means of a plunger working in the chamber, the glass is forced vertically up one passage into a parison mould which comes to rest for a short interval at the exit of the passage. L. D. Soubier[64] has patented an arrangement apparently for the charging of machines in continuous, as against the intermittent, motion for which most types of delivering device apply only.

Two other systems of charging machines automatically with glass are combined with novel features in bottle-blowing machines. The first is that of A. Ferguson.[65] The complete machine consists of three frames or tables, all three synchronised, two of them working in the vertical plane and the third and lowest in the horizontal. The upper vertical frame carries twelve gathering cylinders with movable pistons like syringes, by the action of which glass is drawn up from a trough fed by a tank furnace. The charge thus obtained is then ejected through a funnel into one of the parison moulds on the second table. From the latter the parison is transferred by a fork to the finishing moulds. The second system is due to E. T. Ferngren.[66] In this arrangement the parison moulds are fed from below. A bent channel, forming a continuation of the tank furnace, forms with the parison moulds when in position, the shape of a U. The head of liquid from the furnace forces the glass up into the mould. Between the bottom of the mould and top of the channel is an adjustable plate to cut off the flow during the rotation of the machine.

Improvements in the Westlake bulb-blowing machine[67] may be

[60] E.P. 160,967.
[61] E.P. 142,365.
[62] E.P. 142,765.
[63] E.P. 151,149.
[64] U.S.P. 1,356,174.
[65] E.P. 154,252.
[66] U.S.P. 1,328,273.
[67] E.P. 142,765.

noted, as also the application by A. Kadow[68] of the principle of part of that machine to the pressing of heavy articles of glassware. Very small electric bulbs made from glass tubing may be made automatically by means of the machine devised by G. A. Leiman.[69] The automatic removal of the heavy part of the neck of an electric bulb is accomplished by a cracking-off machine patented by the General Electric Co.[70] The bulbs are mounted necks uppermost on a rotating frame, with intermittent motion. They are brought into contact with a flat flame at one station and immediately afterwards against a moistened sharp chilling wheel, subsequent to which the cracked top is removed by a projecting rod or striker.

Attention may be directed to the glass vial machine of G. P. MacNichol[71] in which small vials are made from glass tubing.

Various methods have been devised with the view of improving the methods of drawing sheet glass direct. Some arise from the desire to advance the Libbey-Owens process, avoiding the marking of the sheet in the early stage during which it is first drawn vertically and then bent over a roller. J. P. Crowley[72] designs an arrangement in which a clay roller actually dips in the drawing trough and by its rotation gathers a layer of glass, which is then delivered to a drawing point whence the sheet is drawn away horizontally. M. J. Owens[73] attempts to deal with the same problem by reducing the temperature of the glass just before it passes over the roller, whilst, after this stage, the sheet is subjected to flattening by an endless chain of wooden rollers. In the same process H. S. Campbell[74] proposes to draw the sheet from the trough by grippers of carbon carried by endless chains. Reference may also be made to alternative processes by J. Whittemore[75] and J. P. Crowley.[76] H. G. Slingluff[77] deals with devices for controlling the temperature of the glass in the drawing part of the tank furnace.

The entirely vertical drawing system for flat sheet, like the Fourcault, which is now being exploited not only on the Continent but also in Japan, and for which American rights have recently been acquired, has received attention from B. G. Bealor.[78]

[68] U.S.P. 1,264,085
[69] U.S.P. 1,342,821
[70] E.P. 160,967.
[71] U.S.P. 1,343,179
[72] U.S.P. 1,328,268
[73] U.S.P. 1,345,628
[74] U.S.P. 1,355,449
[75] U.S.P. 1,328,864
[76] U.S.P. 1,342,533
[77] U.S.P. 1,376,975
[78] U.S.P. 1,331,796

Sheet glass production by flowing methods has been devised by E. Dauner,[79] the glass from a specially-constructed forehearth flowing down both sides of a specially-constructed slab, and after uniting at the lower edge, the stream is drawn away in a sheet. Somewhat similar is the proposal of J. Whittemore.

An ambitious scheme for the mass production of lens blanks is that of H. W. Hill.[80] The apparatus involves heating weighed pieces of the glass in a heating chamber on a rotating table; after being brought to the plastic state these pieces are puddled to remove striæ and bubbles. They are then ejected from the table to a heated conveyor, whence they are carried and deposited in press moulds on a rotating table and subsequently automatically conveyed to the annealing furnace.

[79] E.P. 159,114.
[80] U.S.P. 1,332,724-5.

REFRACTORY MATERIALS.

By W. E. S. Turner, D.Sc., M.Sc., F. Inst. P.,

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The past year has been fruitful in most of the fields of refractory materials investigated, and some researches of quite fundamental importance are to be noted. Several subjects appear to have received special attention and reference may be made particularly to refractoriness under load, the study of plasticity, and the investigations on porosity. As some of the empirical methods of testing frequently employed have been challenged it would be well to have revised and re-issued from time to time standard methods modified according to the most recent investigations.

General Properties of Refractory Materials.

H. S. Houldsworth and J. W. Cobb[1] have considerably extended their previous studies on the reversible thermal expansion of various refractory materials after being heated to definite temperatures. The thermal expansions were measured at varying temperatures from the normal room value up to 1000° C., and the various test pieces had previously been fired at temperatures of approximately 980°, 1280°, 1410°, and 1530° C. Kaolin and bauxitic fireclay, as well as magnesia brick, carborundum, and alumina with 10% of ball clay had a regular rate of expansion. Fireclays and glass pot mixtures after calcination at 980° or 1280° showed a large expansion between 500° and 600° C. due to contained quartz, and on cooling, the contraction in that region was greater than the corresponding expansion. After being fired at 1280°, the expansion between 100° and 250° exceeded the average. After calcination at 1410° or 1530° these irregularities disappeared, and on reaching the incipient vitrification stage a linear expansion similar to that of kaolin was obtained. The change from the irregular to the regular expansion is due to destruction of the free quartz, and the rate of destruction depends on the size of the quartz grains. A mixture of kaolin and amorphous silica with 4% of soda, after being fired at 980° or 1280° showed regular expansion.

An apparatus has been designed by E. Rengade and E. Desvignes[2] for determining the hardness of refractory materials at high

[1] *J. Soc. Glass Tech.*, 1921, **5**, 16; *J.*, 1921, 510A.

[2] *Comptes rend.*, 1921, **173**, 134; *J.*, 1921, 585A.

temperatures. A cone of Acheson graphite was employed to produce an impression on the refractory sample heated in an electric furnace, the pressure used being 10 kg. applied for 10 minutes. Progressive softening occurred with rise of temperature. High alumina content did not appear to influence the extent of the impression, but with alkalis it increased. No impression was made on silica bricks up to a temperature of 1600° C., although above, the adhesion of the grains diminished rapidly.

The heat transmission of brick and high-temperature insulating materials has been investigated by R. H. Horning.[3] A test-piece was heated electrically by coils of wire in contact with it. The cool end rested on a water-cooled plate, baffles causing the water to flow in a zigzag path across the plate. Only the heat passing through the central part of the heated area (about one-ninth of the whole area) was measured, the quantity being obtained from the current and fall of voltage in the central heating coil. The temperature of the hot face was measured by a thermocouple embedded in it, and the average temperature of the water entering and leaving the cooling plate gave the temperature of the cool face. By replacing the cooling plate by electrically-heated coils of wire, a constant difference of temperature was maintained between the faces and the heat transmission measured for different temperatures of the hot face. The materials examined, arranged in order of decreasing thermal conductivity, were magnesia brick, silica brick, vitrified building brick, firebrick, re-pressed burned kieselguhr brick, natural kieselguhr brick perpendicular to grain, "nonpareil" insulating brick, and "nonpareil" high-pressure block. The conductivities increased with rise of temperature up to 1500° F. (815° C.).

One of the most important properties of refractory materials as regards their industrial application is the behaviour under load at high temperatures. K. Endell[4] found that according to their behaviour when heated under a pressure of 1 kg. per sq. cm., refractory materials might be divided into four groups:—

(1) Fireclay bricks with a refractoriness of about cone 33 (1730° C.) began to soften at 1300° C., a 50-mm. cylinder being reduced to 30 mm. in a test lasting 4½ hrs., in which the maximum temperature reached was 1500° C. Bricks containing very plastic clay softened at 1150° C.

(2) Magnesite bricks with a refractoriness above 2000° C. began to soften at 1500° C. on account of the binding agent. A 50-mm. cylinder was reduced to 10 mm. in height in a test lasting 4¾ hours, the maximum temperature attained being 1650° C.

[3] *J. Amer. Ceram. Soc.*, 1920, **3**, 865; *J.*, 1921, 46A.

[4] *Stahl u. Eisen*, 1921, **41**, 6; *J.*, 1921, 347A.

(3) Silica bricks with a refractoriness of cone 35 (1750° C.) did not soften below 1650° C., but broke in pieces in $4\frac{1}{6}$ hours at a maximum temperature of 1680° C. The actual deformation was small.

(4) Carbon bricks with a refractoriness above 2000° C. did not soften under pressure, and apart from a slight loss in volume (about 4%) due to some of the carbon burning away, the cylinders were not affected in a test of five hours in which a temperature of 1720° C. was reached.

The subject has been carried a stage further by V. Bodin,[5] who has determined the resistance to crushing of samples of clay, bauxite, silica brick, carborundum, fused quartz, impure zirconia, magnesia, and chromite bricks. A cube 2 cm. square of the material was placed between two cylindrical blocks, the lower one fixed, the upper one capable of vertical movement. The relationship between crushing load and temperature showed that for silico-aluminous and also silica products, a minimum occurred in the curve at a temperature of about 800° C., after which the crushing load rose to a maximum point at about 1000° C. These results held good for two out of three clays tested, bauxite and carborundum and impure zirconia. A minimum and a maximum point were observed also with fused quartz and silica bricks. The resistance to load tended towards zero with all products tested at about 1600° C., whilst all tended to become plastic or semi-plastic above about 1200° C. The author also found that for bauxite, the crushing load for material fired at 1500° C. was much greater than when fired at 1300° C., thus confirming an observation of Le Chatelier that increased firing temperature increased the refractoriness of a clay.

The testing of refractory materials at high temperatures is frequently interfered with by the influence of the atmosphere in the furnace. In this connexion a phenomenon of very general interest was observed by L. Bradshaw and W. Emery,[6] when attempting to measure temperatures of operations in which coal gas was an active agent. It was found that Seger cones heated in a stream of coal gas became covered with a hard refractory casing of carbon, and remained erect even when fusion of the interior took place leading to the flowing out of a vitreous discharge. The deposition was found possible in all cases where the temperature exceeded 950° C.

Whilst dealing with the influence of the atmosphere it is interesting to direct attention to the testing-furnace designed by W. M. Hepburn.[7] It consists of a surface-combustion furnace lined with

[5] *Trans. Ceram. Soc.*, 1920-21, **21**, 56; *cf. J.* 1921, 213R.

[6] *Gas J.*, 1921, **155**, 159; *J.*, 1921, 624A.

[7] *J. Amer. Ceram. Soc.*, 1921, **4**, 755; *J.*, 1921, 891A.

alundum, fed by seven burners supplied from a mixture box in which an explosive mixture of gas and air was made by a special inspirator, which melted down cone 36 in one hour, using 156 cub. ft. of town's gas. The maximum temperature (3400° F.) attained was within 200° F. of the theoretical maximum. The advantages claimed are simplicity, low fuel consumption, ease of observation and measuring temperatures, and ability to produce a neutral, reducing, or oxidising atmosphere.

A simple form of gas-fired furnace for use in testing the modulus of rupture of refractory materials was built by S. F. Walton[8] in cylindrical form of carborundum bricks backed by 1½ in. of rammed kieselguhr and 4½ in. of firebrick. The gas ports were set tangentially to the wall. For making the cross breaking tests a lever arrangement was used, one end of the lever pressing through a knife edge of refractory material on the test-piece which rested on knife edges embedded in the floor of the furnace. The other end of the lever was connected with a chain jack having a handle fitted to the sprocket wheel and set on a platform scale. A bucket hung from the balance arm of the scale was loaded by water from a Marriotte bottle.

In an interesting paper by H. Wilson[9] a detailed description, with drawing, is given to show the use of oxy-acetylene gas in a small furnace for using refractory cones. The advantages claimed are: (1) simplicity of construction, operation, and repair; (2) ease of control; (3) high temperature obtainable; (4) oxidising atmosphere; (5) comfortable working conditions; (6) portable character of the furnace. The following change is suggested in the Ceramic Society's specified rate of heating for cone fusion tests:—"The rate of heating shall not exceed that corresponding to one-half a cone (approximately 10° C.) per minute within a range of ten cones below that of the final fusion cone, and this rate shall preferably be decreased to one cone per five minutes within two cones of the final cone of fusion."

Silica Refractories.

The possibility of preparing high-grade silica brick from quartzite rock has been examined by E. Lux,[10] who found that silica bricks could be made from quartz rock of a quality corresponding with those made from tertiary quartz. These bricks showed under the microscope a high degree of transformation, even of the large quartzite grains. Such a transformation was effected in the case of quartzite rock by a high burning temperature as is employed in America. The degree of transformation of German silica bricks

[8] *Ibid.*, 1920, **3**, 833; *J.*, 1921, 10A.

[9] *Ibid.*, 1921, **4**, 835.

[10] *Stahl u. Eisen*, 1921, **41**, 258; *J.*, 1921, 390A.

was usually of a much lower order, but microscopical examination of the better bricks showed that by arranging the method of manufacture to suit the raw material, a brick might be made which is not inferior to those prepared from tertiary quartz.

K. Endell,[11] in this connexion, has made a comparative study of American and German quartzites as raw materials for the silica brick industry. The chemical composition, cone fusion temperatures, microstructure in the raw state and after successive firings, and velocity of inversion of successive firings, were determined. After a single firing to 1435° C., the German erratic block quartzites of the tertiary age showed a much greater expansion than the American quartzites. Hessian quartzite resembled the American. The use of the German erratic block quartzites for the manufacture of silica brick of the highest quality was the more economical, both in preparation and burning costs, as compared with the American quartzites.

Observations were made by D. W. Ross,[12] during an extended period, on the silica bricks in the crown of a tank furnace used in the manufacture of bottle glass. It was found that great care was necessary in heating up a new crown due both to the large expansion of the whole crown and to unequal expansion from place to place, some portions expanding considerably more than others. After having been in use for 18 months (or more) a crown could usually be cooled without disruption if the temperature did not drop too suddenly after the heating was stopped. On reheating, the crowns only expanded one half as much as they did in the first heating and local non-uniformity was absent. When a crown had been cooled after being in use for 18 months a large percentage of the bricks were broken in two or contained a source of weakness approximately midway between the inside and outside of the crown. Miscroscopical examination of the bricks after 18 months' service indicated that they were practically all tridymite whereas the unused bricks were largely cristobalite and quartz.

The Rheinische Stahlwerke[13] has carried out comparative tests on each of two batteries of coke ovens, one made of silica bricks (95% silica) with lime bond, and the other of ordinary clay bonded firebricks having 79–81% of silica and 15–17% of alumina. The former bricks were much more resistant to corrosion from salty and wet coals, to slagging and fusing, and to mechanical abrasion. Also, contrary to expectations, the yield of sulphate was not impaired. The coke from the silica brick oven was of better appearance and considerably harder than that from the firebrick

[11] *J. Amer. Ceram. Soc.*, 1921, **4**, 953.

[12] *Ibid.*, 1921, **4**, 65; *J.*, 1921, 218A.

[13] J. Enzenauer, *Stahl u. Eisen*; *Iron and Coal Trades Review*, 1921, 102, 232.

ovens. The economic efficiency of the plant was high. Numerical data are given, illustrating the difference between the working of the silica and firebrick ovens.

In a study of unfired silica bricks, the following properties of silica bricks made in a manner similar to sand-lime bricks, were studied by P. Schneider[14]: compression strength, volume shrinkage, density, percentage absorption, and softening point. The bricks were built into the furnace in the unfired state. Lime and fireclay grog tended to decrease the refractoriness too much, whilst clay, used together with lime, retarded the cementing action, preventing to some extent the formation of calcium hydro-silicates The following method of making silica brick is recommended by F. Orth.[15] A mixture of pure silica (the largest particles passing a 40-mesh screen and the whole graded so as to secure a minimum percentage of voids) with 2–5% of hydrated lime, is moulded, treated with steam at a pressure of 125 lb. per sq. in. for ten hours and afterwards fired for eight days at 2800°–3000° F. (1540°–1650° C.).

R. Wietzel[16] has studied the stability relations of the glass and crystal phases of silica. The heats of crystallisation of quartz, cristobalite, and chalcedony were determined and also their mean specific heats from very low temperatures up to the melting point. Variations in the transition temperatures of quartz and cristobalite were found to depend on the state of division of the material. With very finely divided quartz the transition point could hardly be detected. Chalcedony is not a distinct form of silica, but is microcrystalline quartz. The melting point of cristobalite is 1696° C. Quartz can be melted without conversion into cristobalite; its melting point is between 1600° and 1670° C.

Fireclay Refractories.

Research into the properties of fireclay refractories has not diminished but has tended to increase. E. M. Firth and W. E. S. Turner[17] have continued their investigations[18] of British fireclays and have given the shrinkages, porosities, etc., for the clays after firing to 1500° C.

The shrinkages of some kaolins and clays were measured by A. Bigot[19] on slabs of the prepared clays or kaolins: (*a*) when the finely powdered materials were made into slabs without pressure,

[14] *Tonind. Zeit.*, 1921, **45**, 452.

[15] U.S.P. 1,363,264; *J.*, 1921, 149A.

[16] *Z. anorg. Chem.*, 1921, **116**, 71; *J.*, 1921, 511A.

[17] *J. Soc. Glass Tech.*, 1921, **5**, 268; *J.*, 1921, 891A.

[18] See *J.*, 1920, 628A.

[19] *Comptes rend.*, 1921, **172**, 755; *J.*, 1921, 302A.

(*b*) when the slabs were moulded under pressure. They were compared also with slabs prepared from powdered quartz, felspar, and talc. These last-named materials gave slabs which, on drying at 110°, lost weight but did not contract, finally falling to powder. With the (*a*) samples, it was found that contraction ceased before the weight became constant, the author supposing that, of the water added to the clay, part helped to swell the colloidal particles and part was merely interposed between the particles. Shrinkage ceased, on this view, when the colloidal water had been removed. Tests made with slabs moulded under pressures of 170 kg. and 370 kg. per sq. cm. led to the conclusion that increase of temperature and pressure during moulding diminishes both the colloidal and the interposed water. In these cases, shrinkage ceased at an earlier stage than when the slabs were made without pressure.

In a continuation of the investigation,[20] Bigot measured the variations of volume with temperature of slabs of various clays and bauxities, the slabs being prepared under a pressure of 800 kg. per sq. cm. The conclusions drawn were that all bauxities, kaolins, and clays which contain free silica, commence to shrink below 1000° C. All those which expanded below 1000° C. contained free silica. Whilst bauxities do not rapidly expand before reaching the fusion point, clays and kaolins do. The expansion is regarded as due to the evolution of gases which are trapped in the vitreous silicates.

R. F. Geller[21] has studied the effect of time on the drying shrinkage of three shales, two ball clays, and one fireclay, samples of which were thoroughly worked, and then made up into cubes. It was found that the drying time depended largely on the water content, although the structure of the clay was also of considerable influence. The total shrinkage was proportional to the water content, but was not influenced by the rate of drying.

Porosity, a property of refractory materials which is of far-reaching importance, is receiving extended treatment at the hands of E. W. Washburn and his colleagues. In his introductory paper[22] the author briefly outlines the significance of porosity. The requirements of an engineering testing method are stated to be simplicity, rapidity, and convenience with no more accuracy than practical considerations justify. There should, however, also be available a standard reference method, that is, a laboratory method where accuracy is the main requirement. Six types of pores are described and the process of absorption under various conditions is analysed. Definitions are proposed for the terms permeability, penetrability, absorptivity, porosity, bulk density, closed pore

[20] *Ibid.*, 1921, **172**, 854 ; *J.*, 1921, 302A.
[21] *J. Amer. Ceram. Soc.*, 1921, **4**, 282.
[22] *Ibid.*, 1921, **4**, 916.

space, and "cracks" and "holes," and methods of measurement are suggested.

In conjunction with F. F. Footitt,[23] Washburn has made a thorough investigation of the use of water as an absorption liquid for the determination of porosity. He states that the ordinary immersion method and simple immersion in low vacua without boiling are unreliable. Absorbed water vapour may cause errors up to 2% in the porosity value. Perfectly dry fired clay will remove water even from concentrated sulphuric acid and from fused calcium chloride. Boiling in water at atmospheric pressure produced a gradual and continuous rehydration of the clay, and errors from this source may amount to 3% besides the error from dissolved material, which may amount to 2% during a three hours' boiling.

A vacuum method of saturation is described in which water may be employed as the saturation liquid under conditions where the above sources of error are reduced to a minimum; the method is not, however, recommended as a primary standard. It is shown from theoretical considerations that a soaking period is necessary and methods are given for calculating and for measuring the minimum soaking period required for a given test piece and a given liquid of known penetration.

The use of petroleum products as absorption liquids has been similarly investigated by Washburn,[24] in collaboration with E. N. Bunting. The advantage of petroleum products is that slaking, chemical reaction, adsorption, and solvent action are avoided. Longer soaking time is required, however. Paraffin and vaseline are both materials with a high fluidity when hot, and a comparatively low fluidity when cold. They permit of the surface of the saturated test piece being brought to a definite and reproducible condition with all surface pores full. Paraffin may be used, but vaseline is preferable because it undergoes no change of phase on cooling. A saturation procedure is described and comparative results given. A penetratimeter for determining the penetrativity of liquids is also described. This work is to be continued.

R. M. Howe and his collaborators have continued their valuable work on the spalling of refractory materials. In dealing with tests of firebrick made from ganister, flint clay, and plastic clay mixtures, Howe[25] investigated several properties. Five experimental batches of firebrick were made by mixing various proportions of ganister, flint clay, and plastic clay in such a way as to vary the silica content from 53 to 77% and the alumina content from 43 to 20%. The fusion points were found to be only slightly lower than those of corresponding pure silica-alumina mixtures. Load tests at high

[23] *Ibid.*, 1921, **4**, 961.
[24] *Ibid.*, 1921, **4**, 983.
[25] *Ibid.*, 1921, **4**, 206; *J.*, 1921, 259A.

temperature showed that the behaviour under compression does not depend on chemical composition so much as on other factors such as the temperature of burning. The resistance to spalling, as tested by alternate heating and dipping in cold water, was found to decrease as the temperature of burning was increased from 1300° to 1400° C. The higher silica bricks were relatively more resistant at the lower temperature, but not so at 1400°. Therefore the substitution of ganister for flint clay increases the resistance to spalling at moderate operating temperatures, but is of no advantage at 1400° C. or above.

Together with R. F. Ferguson,[26] Howe studied the spalling of bricks which were heated in the door of a furnace and then rapidly cooled, some by standing in water to a depth of five inches, and others by directing a jet of cold air from a blower on them. In each case the loss in weight due to the detachment of particles was taken as a measure of the amount of spalling. Both spalling tests gave similar results. With bricks made from the same clay, lightly burned bricks spalled less than hard-burned bricks and resistance to spalling was increased by using coarser ground material. These tests led to accurate conclusions where the same fireclays were involved, but misrepresented the facts observed in works service when different clays were concerned. These discrepancies disappeared when the specimens were heated for five hours at 1400° C. before testing. Two fireclays which produced bricks which were very resistant to spalling when in use were characterised by a constancy in porosity over a wide range of temperature, and were therefore considered very resistant to vitrification. When firebricks spalled in service the pieces were usually dense or vitrified. The connexion between vitrification and spalling was established by experiments. Fireclays which underwent slight change in porosity when heated over a wide range of temperature had a very slight tendency to vitrify, and were particularly adapted to the manufacture of non-spalling bricks.

Howe and S. M. Phelps[27] found that in the air-spalling test, burnt bricks with grog had their resistance to spalling increased by 5% for each 1% of grog added. The bricks with grog were, however, more porous and weaker mechanically, but showed less burning and drying shrinkage. The authors do not say that the same results would necessarily obtain with all grogged clays, although with a plastic clay they appeared to do so.

More than one investigator has been interested in the subject of plasticity, and the ageing of clays. R. F. MacMichael[28] concludes, from observations extending over several years, that when water is

[26] *Ibid.*, 1921, **4**, 32 ; *J.*, 1921, 217A.
[27] *Ibid.*, 1921, **4**, 119 ; *J.*, 1921, 217A.
[28] *British Clayworker*, 1920-21, **29**, 163.

added to dry clay, a disruptive force is produced within the mass opposing the cohesion of the clay particles, plasticity resulting from the balancing of these forces. Fluids other than water can produce plasticity, but organic matter and soluble salts are not regarded as essential to plasticity.

The ageing of clay is dealt with by H. Spurrier.[29] Evolution of carbon dioxide was found to continue for over 34 days after pugging, and, like the change of plasticity, to proceed more rapidly between 80° and 90° F. than below 60° F. The effect of replacing water by non-aqueous liquids is to inhibit the development of plasticity altogether. The effect of a dilute solution of hydrogen peroxide is to produce a pronounced increase of viscosity, and also to stimulate the growth of algæ and the consequent evolution of both carbon monoxide and carbon dioxide. It appears probable, therefore, that the change of plasticity of clays with time is due, in some way, to the growth of such algæ. This algæ theory would explain all the facts found. The ratio of the amounts of alumina and silica dissolved by potash was found, for the three clays tested, to decrease rapidly with diminishing plasticity, and therefore might well be used as a quantitative measure of the plasticity.

In a comprehensive survey of the subject of the plasticity of clays, J. W. Mellor[30] states that it is probable, other things being equal, that the distribution of grain size which permits the closest packing of the particles and exposes the maximum surface area, would be most favourable to high plasticity. Agents which cause a clay slip to coagulate enhance the plasticity of clays, while those which deflocculate the clay diminish its plasticity. These effects can be explained by considering the various molecular forces between the clay and liquid molecules. Plasticising agents (*e.g.*, gum, tannin, etc.) probably act indirectly by adsorption, though the plasticity of china clays practically free from organic matter shows that adsorbed organic colloids are not the source of their plasticity. There is an intimate connexion between the plasticity of a clay and its past history with respect to contact with water, which suggests that the clay is slowly hydrated to form a colloid, though no difference could be detected in the plasticity of a clay after removing as much of its colloidal matter as possible.

H. G. Schurecht[31] made experiments on the effects of the firing temperature on the strength of fireclay and stoneware bodies. The cross-breaking strength, porosities, and shrinkages were determined after firing to different temperatures. It was found that, with one exception, maximum strength was developed by firing to cone 8 even when porosity and shrinkage data showed the

[29] *J. Amer. Ceram. Soc.*, 1921, **4**, 113; *J.*, 1921, 217A.

[30] *Trans. Ceram. Soc.*, 1921, **21**, 91; *cf. J.*, 1921, 471A.

[31] *J. Amer. Ceram. Soc.*, 1921, **4**, 366; *J.*, 1921, 511A.

bodies to be over- or under-fired at this temperature. The cause of weakening above cone 8 might be due to the formation of sillimanite. Bodies which developed maximum shrinkage and minimum porosity at cone 8 had a greater ratio of fired strength to dry strength when fired to cone 8 than those which were under- or over-fired at cone 8.

Several papers have been published dealing specially with refractories required for glass-making. D. H. Fuller[32] has made a study of some bond clay mixtures. In attempting to produce results from certain American clays equal to those obtained from Grossalmerode clay in glass pot bodies, the author found it was not possible to duplicate the physical properties, especially the low water of plasticity and low drying shrinkage of the Grossalmerode clay. Several of the mixtures, however, gave better results as regards resistance to corrosion of glass batch than the one containing the Grossalmerode clay.

The raw materials used, the methods of grinding and mixing the raw clay and grog, and the way in which the pots are built and dried are briefly described by W. K. Brownlee and A. F. Gorton.[33] The authors emphasise the importance of handling the pots gently, and of storing them in a warm and dry place. The precautions to be taken in preheating pots in arches are discussed at length, for this is the critical period in the life of the pot The batch should be properly crushed and mixed and should either be preheated or loaded in gradually; and the furnace temperature should be carefully regulated. It is particularly urged that the technical treatment of pots in the glass works be entrusted to a man trained in ceramics and physical chemistry. After discussing the usual design of arches for heating glass melting pots, the authors suggest improvements as to firebox locations, construction of walls, door, etc.

Dealing with the proportional dimensions of wide and low glass-house pots, J. Baldermann[34] argues that the most rapid and economical melting of a glass batch in open pots is accomplished by the use of comparatively low and wide pots. The internal dimensions of the pots recommended range from 1·51 m. at the top to 1·41 m. at the bottom, and 0·535 m. in depth to 0·82 m., 0·72 m., and 0·42 m., respectively, the thickness of the pot wall ranging from 120 mm. to 90 mm. correspondingly. The capacity of the first pot is given as approximately 45 cwt. of batch, and of the second 9 cwt.

There have also been published a number of researches on various other points connected with fireclay refractories.

[32] *Ibid.*, 1921, **4**, 902; *J.*, 1922, 101A.

[33] *Ibid.*, 1921, **4**, 97.

[34] *Sprechsaal*, 1920, **53**, 2, 11.

The tests on clays are unfortunately empirical and different investigators do not all use the same tests. R. F. MacMichael[35] describes a series which he states have given satisfactory results in practice over a considerable period. General appearance and structure, working properties when crushed, pugged, forced through dies, plasticity when made to a standard viscosity, wet strength, drying and firing shrinkage, transverse and breaking weight, working, loss of weight, porosity, density, and refractive index, all are included and directions for their application stated.

W. C. Hancock[36] has shown by using a plastic Stourbridge clay, to which varying amounts of grog were added, that the amount of tempering water required diminishes as the percentage of grog increases, but increases when the grog is made finer in grain.

J. W. Mellor, N. Sinclair, and P. S. Devereux[37] found that clays gradually lose some of their so-called combined water at ordinary temperatures. This water is reversible and is restored in a moist atmosphere, showing that no drastic change has occurred in the structure of the clay molecule. This change is totally different from that which occurs when water is expelled at higher temperatures. This "overdried" clay has some important properties. The resorption of water is so very slow, and it requires so long a time to restore the original plasticity that the working qualities, plasticity, shrinkage, etc. of certain troublesome clays can be modified and regulated by desiccation. The dried clay approaches the condition of many unweathered fireclays in requiring exposure to a moist atmosphere for a long time before the original plastic condition is resumed. The custom of seasoning glass pots for a few months in a warm dry place may not really be so redundant an operation as might at first sight be supposed. From this point of view the storing of clays in a warm dry spot is not conducive to their subsequent working in their most plastic state.

The water-smoking behaviour of two plastic brick clays, one shale, and one fireclay has been studied by R. F. Geller[38] by heating 4-in. cubes at different rates, two thermo-elements being buried in the brick and two others placed against the exterior surface. To save time in water-smoking the ware should be previously dried not far from 100° C., good circulation should be provided in the kiln, and the temperature of the interior of the product should not lag appreciably behind that of the kiln. It should be possible to water smoke heavy clay products in 15 hours with a heating rate of 20° C. per hour.

[35] *British Clayworker*, 1920, **21**, 29, 189.
[36] *Trans. Ceram. Soc.*, 1919-20, **19**, 149.
[37] *Ibid.*, 1921-22, **21**, 104.
[38] *J. Amer. Ceram. Soc.*, 1921, **4**, 375; *J.*, 1921, 511A.

A method is described by H. G. Schurecht[39] for determining the rate of sedimentation of clays by measuring the suspended weights of a glass plummet in a clay slip at different intervals of time. The specific gravity of the slip remaining in suspension may be calculated as follows :—$S = (P_d-P_s) \div (P_d-P_w)$, where S is the specific gravity of the slip, Pd the dry weight of the plummet in grams, P_w the suspended weight in distilled water, and P_s the suspended weight in the clay slip. The average weight of clay per c.c. is calculated as follows :—$C_w = D(S - d) \div (D - d)$, where C_w is the average weight of clay per c.c., D the specific gravity of the clay, and d the specific gravity of water. It is impracticable to separate by elutriation clay particles smaller than 0·003 mm., which constitute 50–100% of many clays. It is possible to classify particles as small as 0·0001 mm. by the plummet sedimentation method, and the results are more uniform than those obtained by elutriation.

According to W. H. Grant[40] the failure of firebricks in oil-fired furnaces results from : (1) spalling and falling of side-wall bricks ; (2) disintegration of bricks in the direct path of the flame ; (3) glazing of the surface with green glaze which penetrated and weakened the brick ; and (4) erosion by flame. A plea is made for more research in the field.

Basic Refractories.

H. G. Schurecht[41] has made extended experiments in the dead burning of dolomite and magnesite. Dolomite is difficult to burn dead, because the absorption of moisture from the air produces a gradual slaking, due, probably, to the hydration of lime and various lime compounds, and this tends to cause disintegration. With all the fluxes tried, 100-mesh raw material gave greater resistance to slaking than 8-mesh size. This resistance decreased, however, with increasing temperature of calcining by an amount which appeared to depend on the silica and alumina content of the flux, being greatest for basic open-hearth slag and kaolin, less for flue dust and iron ore, and least for roll scale. The stability also varied with the proportions of flux used, being greater, as a rule, for smaller proportions. The shrinkage and porosity curves for mixtures containing flue dust, iron ore, or roll scale were very similar. The higher the proportion of flux, the lower was the temperature required to get maximum shrinkage and minimum porosity. Kaolin and basic open-hearth slag behaved peculiarly in that vitrification depended more on the burning temperature than on the properties of the flux used. It was found that ageing of the wet calcined material was necessary to prevent cracking of

[39] *Ibid.*, 1921, **4**, 812 ; *J.*, 1922, 101A.

[40] *Ibid.*, 1921, **4**, 390 ; *J.*, 1921, 511A.

[41] *Ibid.*, 1921, **4**, 127 ; *J.*, 1921, 218A.

the bricks upon drying. With 5% of magnesium chloride as binder, comparatively strong bricks were obtained. High shrinkage on firing caused excessive cracking, but the bricks were extremely dense and did not disintegrate until after four to six months. Unfired tar-bonded bricks were made with sufficient strength to stand shipping and with a storage life of about four months. Fired tar-bonded brick showed less shrinkage and cracking than similar bricks made with water. If dipped in tar to protect them from moisture, such bricks would last five or six months before disintegration. It is possible then to make dolomite brick with a storage life long enough to allow shipping and placing in furnaces. Unlike dolomite, magnesite showed less slaking effect the higher the temperature of burning. Roll scale gave greater stability than iron ore, probably because of its lower silica content. The product was comparatively porous and had a low shrinkage even with high proportions of roll scale.

A method of treating refractory oxides and for shrinking magnesia has been patented by L. E. Saunders.[42] For (*a*) shrinking, agglomerating, sintering, or fusing refractory oxides, or (*b*) shrinking magnesia, the material is heated locally by the passage of an electric current through, for instance, a thin carbon rod embedded in the charge above the median horizontal line. The carbon burns away and the charge in the vicinity agglomerates and becomes electrically conducting and then serves to carry the current.

On the basis of practical experience the preparation and use of mixtures of dolomite and tar for converters are described by M. Backheuer,[43] and a method is indicated for burning the plugs, rendering them free from cracks and giving greater durability to the packing.

In dealing with fireclay, silica, magnesia, chrome, bauxite, zirconia, carborundum, and alundum refractories for the electric furnace, R. M. Howe[44] gives figures for fusion points, temperatures at which the refractory failed under a load of 50 lb. per sq. in., thermal conductivity at 1000° C., and specific heat at 100° C., and indicates the resistance of each to spalling. He also gives directions and advice for furnace construction and control.

A number of patents have been issued covering the manufacture of refractory materials for furnace linings. A. Rollason[45] suggests crushed dolomite or magnesite mixed with 5–10% of crushed basic slag, passed through a basic-lined rotary kiln internally fired to approximately 1800° C. If annealed out of contact with air it "knits together" better.

[42] Assr. to Norton Co., U.S. 1,352,387 and 1,352,388; *J.*, 1921, 149A.

[43] *Stahl u. Eisen*, 1921, **41**, 954; *J.*, 1921, 587A.

[44] *Chem. and Met. Eng.*, 1920, **23**, 1215.

[45] E.P. 156,447; *J.*, 1921, 149A.

J. F. Mollen and W. W. Pathoe[46] state that refractory material suitable for furnace linings is made by adding a small percentage of common salt to a slurry of raw dolomite and then passing the mixture through a rotary kiln operated at a temperature sufficiently high to calcine the dolomite and drive off practically all the salt.

A monolithic furnace lining or other structure is made, according to J. H. Cumpsty,[47] by arranging suitable metal reinforcement in a mould and filling the latter with a thin cement composed of magnesia and sodium silicate or like binding material, or with a mixture of broken magnesite bricks or magnesite and 10% of sodium silicate. The moulded article is dried and fired and is then ready for use.

Other Refractories.

The investigation of the physical characteristics of specialised refractories has been continued by M. L. Hartmann and W. A. Koehler,[48] who have determined the transverse breaking strength of ten commercial refractory bricks at 20° C., and at 1350° C. All materials except two specimens of bonded carborundum showed a great reduction in strength at the higher temperature. The values for the modulus of rupture in pounds per square inch at 20° C. and 1350° C. respectively for specimens of the materials mentioned, were: bonded carborundum-carbofrax A 2103, 2274; carbofrax B 2651, 2129; carbofrax C 2215, 1918; silica No 1 608, 145; silica No. 2 491, 178; magnesia 1388, 136; fireclay grade A 665, 113; bauxite 1315, 99; chrome 1392, 22.

The preparation of zirconia from Brazilian ore and a new method for determination of zirconia is described by E. C. Rossiter and P. H. Sanders.[49] In the extraction of zirconia in a pure state from its ores, one of the chief difficulties is the complete separation from iron and alumina. This paper describes a simple method for the separation, one which has been found to give practically quantitative results. The method is based on the precipitation of the zirconia as a basic sulphate in which the ratio of zirconia to sulphuric acid is expressed by the formula $5ZrO_2,2SO_3$.

M. Sheppard[50] has studied the effect of calcined zirconia on zirconia cements. Seven refractory cements were made having compositions of zirconia 90% and plastic clay 10%. The shrinkage was found to be excessive in a cement containing raw zirconia and clay. The addition of 50% or more of calcined zirconia practically eliminated this shrinkage and the cracking which accompanied it. Draw trials showed that the cement became strong at 1200° C.

[46] U.S.P. 1,365,336; *J.*, 1921, 149A.

[47] E.P. 155,315; *J.*, 1921, 82A.

[48] *Trans. Amer. Electrochem. Soc.*, 1921, 129; *J.*, 1921, 771A.

[49] *J.*, 1921, 70T.

[50] *J. Amer. Cer. Soc.*, 1921, 4, 662; *J.*, 1921, 891A.

and that it was very strong when burned at 1700° C. Load tests on piers at 1500° C. showed that joints of these cements did not fail in any manner at this temperature. An industrial test of zirconia cement used as a wash for bungs in a malleable iron furnace showed that the life of a bung was increased about 25% by the use of a zirconia wash.

Patents granted to the Carborundum Co., Ltd. included the following: F. J. Tone [51] makes a highly refractory material consisting essentially of a burnt mixture of zirconia and sillimanite. Others by O. Hutchins [52] are for (*a*) a highly refractory material consisting essentially of a burnt mixture of zirconia and alumina, and (*b*) a mixture of zirconia and chromite. M. L. Hartmann [53] describes a refractory containing carborundum and a bonding material containing mixtures of zirconium and aluminium silicates. S. C. Linbarger [54] outlines the production of a refractory article which is built up in layers, one outer layer having fireclay as its predominating element, and the opposite outer layer, forming the facing of the article, having silicon carbide in proportions ranging from 50 to 100%. In order to avoid spalling the amount of silicon carbide in the intermediate layers is proportioned so that the coefficient of expansion varies gradually on passing through successive layers.

Graphite for crucibles has received considerable attention. F. G. Moss [55] has dealt with the refining of Alabama flake graphite for crucible use. Investigations on refining crude graphite concentrates showed that no one refining treatment is equally applicable to all concentrates on account of the different characteristics of the crude graphites and their impurities. When the impurities are free or soft, they can easily be separated by grinding, but hard impurities interlaminated with the graphite are more difficult to separate. An aspirator and pneumatic jig are only useful for removing the coarse, hard, and free impurities. It is possible by the refining method suggested to obtain a final product with over 90% of carbon.

G. H. Dub [56] published tentative specifications, suggested by the Columbus Experiment Station of the U.S. Bureau of Mines, for No. 1 flake graphite, as follows: The graphite carbon content determined by weighing the residue left after heating the dried sample for three minutes at 800° C. should not be less than 85%. The cumulative percentage residues on a series of screens should be: 35% on 35 standard mesh; 50% on 65 standard mesh, and 100%

[51] U.S.P. 1,362,274; *J.*, 1921, 82A.

[52] U.S.P. 1,362,316-7; *J.*, 1921, 82A.

[53] U.S.P. 1,376,091; *J.*, 1921, 434A.

[54] Assr. The Carborundum Co., Ltd., E.P. 168,261; *J.*, 1921, 735A.

[55] *U. S. Bureau of Mines Bull.*, **112**, 1920, 46; *J.*, 1921, 81A.

[56] *Ibid.*, 1920, **112**, 38; *J.*, 1921, 81A.

on 100 standard mesh. The permissible allowance is not more than 3% through a 100-mesh screen.

Two methods for making graphite crucibles are described by J. H. L. De Bats.[57] In the first, non-ferrous metal is mixed with the material containing clay from which the crucible is made, giving, in use, a surface coating of metallic silicate, and in the second, finely-divided metal of the aluminium-magnesium group is mixed with material containing clay used for making crucibles; the latter may be burned shortly after moulding.

[57] Assr. to the Lava Crucible Co. of Pittsburgh, U.S.P. 1,374,909 and 1,374,910; *J.*, 1921, 434A.

CERAMICS AND BUILDING MATERIALS.

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The past year does not appear to be marked by any work of outstanding significance, though the literature published during the period, while not extensive, contains many interesting and important data. Research work seems to have been applied more generally to the solution of specific commercial problems, the fundamental scientific principles, affecting the whole field of ceramics, having received rather less attention. This was, perhaps, the natural consequence of the unsettled economic conditions, which have prevailed universally throughout the post-war period. The scarcity of coal, for instance, is responsible for the remarkable amount of space devoted by the technical journals to the subject of fuel economy in all its aspects.

The physico-chemical problems concerning the nature of soils have, of late, received much attention. Some of these—in particular those dealing with the effect of grain size and the quantitative disposition of colloidal matter, bearing, as they do, on the fundamental properties of clays—are of special interest to the ceramist.

In a bulletin, not previously mentioned in this summary of progress, Sven Odén[1] discusses in an able manner the various theories postulated in explanation of the constitution of clay. As the result of his own observations, he defines clay as "A disperse formation of mineral products in which particles smaller than 2μ predominate. Amongst these mineral fragments may occur quartz, felspar, mica, and others, as well as their various decomposition products." Also, "While in most colloidal media the disperse phase constitutes the minor part of the system, in clays the disperse phase predominates."

A. Benecke[2] has studied the relation between the colloidal matter in clays and plasticity. Several experiments on the adsorptive capacity of clays are cited. The author states that when specified salt solutions are allowed to stand in contact with clay, definite amounts of the basic ions are adsorbed. In his remarks on the action of electrolytes upon clay slips, he again draws attention to the fact that the phenomena of deflocculation and coagulation occur in phases; the curves indicating the progress of these phenomena show maxima and minima. He concludes, in his

[1] *Bull. Geol. Inst. Upsala Univ.*, 1916, **15**, 175.

[2] *Sprechsaal*, 1920, **55**, 490.

summary, that the recognition and further investigation of the colloidal nature of clays may lead to a satisfactory scientific method of measuring plasticity.

C. J. Moore, W. H. Fry, and H. E. Middleton[3] have worked out the necessary details of a process for measuring the colloidal content of clays. Their method may be summarised thus: The sample is blunged with water, allowed to settle for a given length of time, the apparently clear supernatant liquor then decanted, centrifuged, and the colloidal matter extracted by dialysis. The behaviour of this so-called "ultra-clay" is typically colloidal; it exhibits a well-defined Brownian movement, and when dried has an exceptionally high mechanical strength. Two methods are indicated, one based on the relative absorption of ammonia after drying at 110° C., and then after heating to 1130° C., and the other on the relative absorption of malachite green after similar treatment. A typical result is:—Colloidal clay, heated to 110°, absorbed 0·1196 g. of dye; untreated clay, heated to 110°, 0·0357 g.; heated to 1130°, 0·0018 g. Assuming that the last figure (0·0018 g.) represents the absorption by non-colloidal matter, then 0·0357–0·0018=0·0339 g. has been absorbed by the colloid. Hence, the ratio of 0·0339 to 0·1196 gives the proportion of colloidal matter present in the clay, in this case therefore, 28·3%. Parallel experiments on similar clays to those used for the dye-absorption test were subjected to the ammonia treatment, with the remarkable result that identical values were obtained in both cases.

A modification of the apparatus designed by Odén for studying the sedimentation of soils is described by H. G. Schurecht.[4] For determining the rate of sedimentation of clays the suspended weight of a glass plummet immersed in a clay slip is determined at different intervals of time. The new apparatus, designed by the U.S. Bureau of Mines, is intended to overcome some of the objections to the Odén and Wiegner methods. It is claimed that particles as small as 0·0001 mm. can be classified by the plummet sedimentation method and that the results are more uniform than those obtained by elutriation.

Many experimenters have used the "Plate theory" in relation to plasticity, so that further investigation of the mechanics of surface friction is welcome. C. Terraghi has determined the character of these forces by a careful study of the behaviour of smooth glass plates in close contact. When exposed to external forces, the effect of interposed water films is very marked. Frictional resistance was found to be due to the presence of microscopic particles deposited between the two surfaces.

[3] *J. Ind. Eng. Chem.*, 1921, **13**, 527; *J.*, 1921, 710A.

[4] *J. Amer. Ceram. Soc.*, 1921, **4**, 812; *J.*, 1922, 101A.

[5] *Phys. Rev.*, 1920, **16**, 54.

In an account of his research on the nature of occluded gases in prepared clays, H. Spurrier[6] has made a valuable contribution to ceramic literature. Clay pugged in the manner described in his earlier communications was found to evolve carbon dioxide continuously for 35 days. A parallel series of trials was conducted at temperatures of 60° F. and 80°–90° F., and it was found that the rate of evolution increased at the higher temperatures. This observation is important, since it was already known that clays stored at a temperature slightly above normal became more plastic than when aged at, say, 60° F. Subsequently, he designed a series of experiments with the object of artificially increasing the plasticity of clay. Water, for instance, was replaced by alcohol, benzene, bromoform, carbon bisulphide, carbon tetrachloride, ether, and sulphuric acid, but none of these substances led to the desired result. He concluded, therefore, that the presence of hydroxyl-ions is an essential factor. Upon adding hydrogen peroxide to various slips, he found that the viscosity and plasticity were increased with a simultaneous growth of green algæ. Owing to the respiration of this filamentous growth, carbon dioxide and carbon monoxide were given off; to maintain continuous growth, further additions of the peroxide had to be made from time to time, the mass finally becoming distinctly plastic. The author concludes that the increased plasticity of stored clays is due to bacterial action (a theory that had been propounded many times previously, and at least one attempt has been made on a commercial basis to increase plasticity artificially by somewhat analogous methods). A comparative measure of plasticity, it is suggested, may be obtained by determining the ratio alumina-silica dissolved by a hot solution of caustic potash. The few experiments recorded appear to warrant further research along these lines, but they are not of such a nature as to justify positive conclusions, little having been added to the results obtained by earlier observers.

J. W. Mellor[7] reviews the modern theories relating to the causes of plasticity and criticises many of the so-called plasticity tests, *e.g.*, dye-absorbing capacity, viscosity of slips, flow under pressure, etc. The property, he points out, is a mechanical one, the resultant effect of a deformation and a pressure, therefore tests which measure only one physical property are not measuring plasticity. He states further that experiments are now being made in which the following factors are noted:—the proportion of water to the clay, the resistance offered to change of shape, the amount of deformation possible without causing the clay to crack; and that the

[6] *J. Amer. Ceram. Soc.*, 1921, **4**, 113; *J.*, 1921, 217A.

[7] *Trans. Ceram. Soc.*, 1921, **21**, 91; *J.*, 1921, 471A.

results will be published later. In the concluding portion of his paper, the author recalls previous experiments carried out by Löwenstein, Bleininger, and Moore, who reported that clays may be partially dehydrated at ordinary temperatures, and that long exposure in a moist atmosphere restores the plasticity. Hence the change may be said to be reversible.

The experiments reported by J. S. Laird and R. F. Geller[8] on the rehydration of clays that had been calcined to temperatures of at least 700° C. are worthy of note in this connexion.

S. Satoh[9] has studied the changes which occur when Japanese kaolinite is heated over a range of temperatures extending from 100° to 1400° C. In the initial experiments he used an apparatus similar to that described by earlier research workers, but finally adopted a differential method. As the furnace containing the kaolinite was heated, the temperature of the specimen was compared with that of a substance assumed inert, such as quartz sand. Minor endothermal and exothermal changes occurred up to 100° and at 100°–300° C. respectively. Further endothermal changes were noted at 450°–650°, and again at 650°–700° C., whilst exothermal changes were indicated at 950° and between 1200° and 1300° C. The author is of the opinion that the kaolinite is dehydrated between 450° and 650° C., and that the change observed between 650° and 700° is the result of the dissociation of the anhydrous kaolinite into free alumina and silica. The polymerisation of alumina occurs at 950° and amorphous sillimanite is formed between 1200° and 1300° C. In support of these assertions he points out that kaolinite becomes isotropic above 900°, and that there is a marked increase in refractivity between 1200° and 1300°. His conclusions as to the formation of sillimanite are somewhat contradictory, since, in his opening remarks, he states that the formation of sillimanite begins near 1400°. Sillimanite has been positively identified in clays not heated to such temperatures as those indicated by Satoh. As W. M. Washburn pointed out in the discussion, quartz cannot be regarded as an inert substance, since it shows a definite endothermal change at 575°. Hence, any conclusions regarding possible changes in kaolinite in the neighbourhood of this temperature are invalidated if a differential method of comparison with the behaviour of quartz be the basis of the experiment.

Radical alterations in the methods of preparing china clay are described in a recent review of the subject.[10] The clayey suspension is removed from the open workings by electrically-driven centrifugal pumps, thus rendering obsolete the button-hole launder, Cornish pumps, etc. Cone-shaped sand settlers are replacing many of

[8] *Ann. Repts.*, 1920, **5**, 208.
[9] *J. Amer. Ceram. Soc.*, 1921, **4**, 182 ; *J.*, 1921, 259A.
[10] *China Clay Trade Rev.*, 1921, **2**, 740.

the older rectangular sand drags. The efficiency of the clay drying process is likely to be increased if the experiments with gaseous and oil fuels now in progress on a works scale are successful.

According to A. S. Watts,[11] chalcedony may be substituted for flint in whiteware bodies. Treated in a similar manner to flint as regards calcination etc., the material would appear to be a suitable ingredient where the usual flints are unobtainable.

R. Twells and C. C. Lin [12] have made an exhaustive study of the effect of replacing free silica in porcelain bodies by zirconia and alumina. The type of porcelain developed by them appears to be very suitable for electrical insulators. Zirconia lowers the maturing point of the body and greatly increases the resistance to rapid thermal changes. Alumina lengthens the firing range, thus giving stability, but increases the liability of the finished product to rupture when subjected to rapid alternations of temperature. The results as regards the effect of the two materials on dielectric strength and toughness are inconclusive. Confirmation of the above data relating to zirconia is found in a later report by R. F. Geller and B. J. Woods,[13] who extended their experiments to include rutile, thoria, and zircon. A series of porcelain bodies were made up, in which these materials were used to replace flint; the amounts used ranged from 27 to 49%, with a simultaneous decrease in felspar content of from 28 to 6%, in every case the proportion of clay remaining constant. Additions of rutile and thoria cause the body to have undesirable properties, without any corresponding increase in mechanical strength or resistance to spalling. Zirconia behaves excellently, and is undoubtedly a desirable constituent in the type of body under review. On the contrary, zircon is unsatisfactory, both from a manufacturing standpoint, and also as regards desirable qualities in the finished goods.

The work reported in last year's summary on the production of "low-fire" porcelains has been carried a stage further by T. Hertwig,[14] who has compounded a series of bodies in which he varied the molecular proportions of the different basic oxides and also the acid ratio in relation to the total RO content. He concludes that a high potash content, coupled with a correspondingly low acid ratio, gives the best results. Reference is made to the "greasiness" which is common in porcelains with a high silica content. This defect has received considerable attention by other ceramists—notably Seger.

[11] *Brick Clay Rec.*, 1921, **59**, 583.

[12] *J. Amer. Ceram. Soc.*, 1921, **4**, 195; *J.*, 1921, 260A.

[13] *Ibid.*, 1921, **4**, 842; *J.*, 1922, 101A.

[14] *Sprechsaal*, 1921, **54**, 11; *J.*, 1921, 148A.

G. Farrant[15] advocates the application of closed-circuit cylinder grinding to the preparation of ceramic body materials. Most of the figures accompanying the paper refer to the grinding of heavy mineral products; the author, however, recognises the fact that the pottery manufacturer requires a totally different quality of fineness from that which applies to industries for which it is sufficient if a material passes a certain specified lawn. In the case of flint, stone, felspar, etc., used for ceramic bodies and glazes, there must be a definite grading of the particles, particularly those ranging between 0·01 and 0·063 mm. in diameter. It is claimed that, by the use of a Hardinge conical cylinder in circuit with a suitable hydraulic classifier, any predetermined grading can be obtained. The principles involved in the use of continuous ball mills of various types have been discussed previously, and there is no doubt that conical ball mills are most efficient mechanically. The particular classifier mentioned by this writer is of the ladder conveyor type, but in the subsequent discussion doubts were raised as to its suitability for the purpose. Considering the tendency of cylinder-ground materials to set on standing, there is a distinct possibility that these fears may be well-founded. Probably a much simpler tubular hydraulic separator could be designed, which would give better results without the elaborate machinery involved in the type suggested. The author states that a Dorr classifier has been ordered for use in a pottery mill, so that the publication of precise data may perhaps be expected later. The closed-circuit system will require considerable modification before it can be used for the grinding of pottery glazes, containing varied proportions of hard, glassy fritt, relatively softer materials, *e.g.*, stone, flint, and also lead compounds with a much greater specific gravity than the remaining ingredients.

B. Moore,[16] in a paper dealing with the question of grain size of body materials, emphasises the fact that, in certain instances, the physical condition of the materials is of greater importance than the chemical composition. The laboratory grading tests are generally carried out in a Schöne elutriator, Schulze funnel, or modifications of these appliances. In any case, the quantities dealt with are small, and the risk of experimental error is such that skilled operators are essential. Furthermore, the time involved in carrying out a test renders the results in many cases of little practical value. The works elutriator described by the author appears to be simple and highly efficient. A pint of slop material can be elutriated, and the result of the test known within four to six hours, and this without the supervision of an expert operator. In the concluding portion of this paper the principles involved in the

[15] *Pottery Gazette*, 1921, **46**, 1796.

[16] *Trans. Ceram. Soc.*, 1920, **20**, 112; *J.*, 1921, 771A.

calculation of surface factors are discussed at length, an earlier research by J. W. Mellor on the subject being recalled. It has generally been assumed that, in a sample containing particles with extreme diameters of 0·01 mm.–0·06 mm., equal weights of particles of 0·01, 0·02 . . . . 0·06 mm. diameter are present. From observations extending over a lengthy period, the author is of opinion that this assumption is totally wrong; he argues that if, for instance, a sample of flint is ground until 50% is finer than 0·01 mm. in diameter, then 50% of the remaining particles will have a diameter of 0·02 mm., 50% of the subsequent remainder one of 0·03 mm., and so forth. Summarising, he states that, in fine grinding, the weight of the finer particles is constantly increasing, with a corresponding decrease in the weight of the coarser fraction. Hence the surface factor, as usually reported, will be lower than it should be. For materials likely to vary in density he recommends that specific gravity determinations should be made and the velocity of the water passing through the elutriator adjusted accordingly. Continuity of sizes is a subject which calls for careful investigation, for, if a definite law could be postulated, by the aid of which the proportions of the remaining fractions could be calculated, given the weight of one fraction, a great step forward would have been taken towards the simplification of factory testing methods.

A. Heath and A. Leese[17] submit some data concerning the effect of the calcination of the flint in an earthenware body. When flints used in whiteware bodies vary in the degree of calcination many troubles may arise if the slop method of mixing be adopted. Boulder flints were calcined in two kilns, in one of which a maximum temperature of 720° C. was reached in 12 hours, the other attaining to a temperature of 1100° in 60 hours. The specific gravities of the resulting calcined materials were 2·481 and 2·312 respectively, whilst the surface factors of the ground materials were practically identical. Two batches of a standard body were made up; easy calcined flint was used in one, and hard-calcined in the other. Distinct variations in firing contraction and porosity were noted, and the harder calcined material showed less inclination to craze. A simple volumeter was described, by the use of which indirect estimation of specific gravities might be speedily effected. Incidentally it was mentioned that calcined flints occasionally exhibit a blue coloration instead of the normal white tint, and it was suggested that this defect might be due to the formation of a compound allied to ultramarine.

Attention is directed by A. S. Watts[18] to the possibility of defects arising from the use of unprecipitated soluble cobalt stain in whiteware bodies. He concludes from his experiments that it is necessary

[17] *Ibid.*, 1920, **20**, 121; *J.*, 1921, 771A.

[18] *J. Amer. Ceram. Soc.*, 1921, **4**, 451; *J.*, 1921, 771A.

to dissolve the salt in water and precipitate the cobalt by the addition of sodium carbonate. As a suitable concentration he suggests that ten parts of cobalt sulphate to 500 parts of water be precipitated by the addition of 5 parts of the alkali. Figures are given relating to the quantities required to neutralise various weights of ball-clay; Watts states that, if more than 15% of ball clay be present in a body, it is impossible to decolorise it completely with cobalt stain. The author claims that the soluble decoloriser may be used for glazes, and suggests that for 100 lb. of a normal glaze about 10 oz. of the solution is required to give a clear white colour. His conclusions as to decolorisation of bodies containing ball clay will be questioned by English manufacturers.

The usual methods adopted for dewatering clay slips (filter-pressing, evaporation, etc.) are notoriously inefficient. This is mainly due to the peculiar behaviour of clayey suspensions. The colloidal nature of pottery clays rules out what, in other industrial fields, are distinctly economical systems, as, for instance, the rotary drum type continuous filter. Centrifuges are unsuitable for compounded bodies, owing to the unavoidable separation and grading that takes place in this type of machine. Electrolytic presses, on the other hand, appear to offer possibilities; it may, therefore, be expected that the costly experiments now in progress will eventually justify the outlay. Meanwhile, modifications of present systems, particularly in the adoption of compressed air as a means of filling filter presses, are materially reducing maintenance charges. A clothless filter-press is reported,[19] but as yet no data concerning its behaviour in practice are available.

High labour costs have, of necessity, directed attention to the efficiency, or otherwise, of the various making processes, and though the published information on the subject is perhaps a little scanty, very real progress is being made. Casting with alkaline slips is becoming general in all branches of the industry. This is particularly noticeable in the heavy enamelled fireclay and sanitary line, whilst in the manufacture of bone china its advantages are now being recognised and exploited. Multiple moulds are used in increasing numbers with good results. Numerous patents have been taken out for jolleying machines, automatic turning lathes, and accessories for placing.

In a valuable paper, A. B. Taylor and E. Irvine[20] publish data relating to porosity, strength, and absorbing power of pottery plasters. In connexion with research work on casting under pressure, they were desirous of producing a mechanically strong mould which, while able to withstand the exceptional pressures, would yet retain sufficient porosity to give the required absorbing power.

[19] O. Frank, G.P. 330,224; *J.*, 1921, 390A.

[20] *Trans. Ceram. Soc.*, 1920, **20**, 83; *J.*, 1921, 772A.

The first series of experiments was designed to determine: (1) the relation between the amount of water used to gauge the plaster and its mechanical strength etc., and (2) the result of employing a 1% solution of borax instead of water. It was found that the borax solution acted as a retarder and permitted a larger proportion of plaster to water to be used. Naturally, the resistance to impact, crushing and tensile strength were increased. The latter portion of this paper deals with the designing of the moulds with reference to moulding under pressure; it was found that those parts which first become saturated with water take up a thicker layer of clay than the remaining surface, consequently greater attention has to be paid to variations in thickness at different points. Allen has proved that in vacuum casting the design of the mould is all-important. The relation between porosity and permeability was also noted; in this connexion it may be pointed out that the method of mixing and pouring would vitally affect the results. Apart from the advantages mentioned by the authors, retarded heavier-gauged mixtures would undoubtedly prove of great service in the manufacture of such articles as mould-makers' cases, where strength and non-absorption are factors of prime importance. Further research along these lines will certainly be of incalculable benefit.

The drying shrinkage of some shales, fireclays, and ball clays has been studied by R. F. Geller.[21] Two-inch cubes were dried in electrically-heated ovens, and in each experiment the time-temperature curve was approximately a straight line. In general, his conclusions confirm the results of other earlier investigations on this subject, and prove that a greatly increased drying rate is possible if the moisture is removed as quickly as it is formed. The fact that an American ball clay, though containing considerably more moisture than an English variety, can be dried more quickly, seemed to cause the author some difficulty. It must be remembered, however, that uniformity of grain size tends to increase the drying rate; and that these two types of clay differ considerably in this respect, has been demonstrated repeatedly in previous work on the tensile strength of American and English clays.

A paper by A. Bigot[22] embodies the results of his observations on the loss of weight and linear contraction of kaolins and other clays during drying. He states that contraction ceased before the clay reached constant weight, and concludes that a portion of the added water combines with, and therefore increases the volume of, the colloidal particles, the remainder merely serving to fill in the interstitial spaces. Evaporation of the "colloidal" water must reduce the volume of the mixture, whereas the loss of the intervening water has no effect.

[21] *J. Amer. Ceram. Soc.*, 1921, **4**, 282; *J.*, 1921, 390A.
[22] *Comptes rend.*, 1921, **172**, 755; *J.*, 1921, 302A.

The need for international standardisation of testing methods as applied to ceramic products is still farther emphasised by the reports issued during 1921. This lack of uniformity among the records renders it unnecessarily difficult to correlate the available data.

China clay producers have an agreed standard of colour, by which any new samples are graded, the price varying directly with the purity of the colour. Ostwald's colorimetric scale, described by W. Funk,[23] would be a suitable one for such standardisation purposes.

Many methods have been proposed for the measurement of translucency. R. Fournier[24] approaches the subject from a distinctly novel standpoint; he takes advantage of the fact that the resistance of a selenium plate located in an electric circuit varies directly with the amount of light it receives. In his instrument the personal factor is entirely eliminated, since the measurements bear a positive relation to the translucency of the sample. He claims, further, that, with slight modification, the instrument can be arranged to measure the reflecting power of any surface. If the apparatus described by Fournier could be modified so as to measure the translucency of porcelain and the reflecting power of pottery glazes, it would be of great service to the ceramic industry.

An improved machine for the measurement of resistance of porcelain bodies to impact is accredited to E. Rosenthal and F. Singer.[25] The instrument is of the pendulum-hammer type, and is giving consistent results. From the description, it appears to be a modification of an Izod impact tester, as used in the engineering industries.

The study of porcelain bodies lends itself to the use of ternary graphical representations, and in a dissertation by V. Pfaff and M. Donath[26] a useful method is outlined. By the use of superimposed triangles the relation between materials, body mixtures, etc. and the theoretical clay, quartz, and felspar contents, can be seen at a glance.

H. H. Sortwell[27] reports the results of his work on the solubility and fusibility of alkaline frits of the type used as a basis for pottery glazes. He indicates clearly and concisely the limits within which frits may be successfully compounded from fused borax, felspar, and lime. The effect of the latter constituent in decreasing the solubility is decidedly marked, though none of the ternary mixtures examined had a really high solubility. The determination of the deformation point was difficult owing to the peculiar behaviour

[23] *Ber. deuts. keram. Ges.*, 1921, **2**, 39.
[24] *Paper*, Feb. 9, 1921, 32; *J.*, 1921, 343A.
[25] *Chem. Zentr.*, 1920, **90**, IV., 675.
[26] *Ber. deuts. keram. Ges.*, 1920, **1**, 21.
[27] *J. Amer. Ceram. Soc.*, 1921, **4**, 446; *J.*, 1921, 772A.

of the high-borax frits. Possibly the results would have been better if each of the mixtures had been previously melted, and the deformation points then determined on the fused material. Further research by the author would be welcome, particularly if he could establish a law governing the deformation point and the viscosity of glaze frits.

The same author[28] has investigated the relation existing between the bases, alumina, and silica in the production of high-fired porcelain glazes. Using a constant RO content he varied the molecular proportions of silica and alumina within wide limits. The experiments prove that the alteration of the silica content has a more pronounced effect upon the range within which good glazes may be expected than is the case with alumina. The effect of increased temperature on each of the glazes is well shown by the diagrams accompanying the paper. At cone 10 there is a large area of crazing glazes and a smaller area of bright glazes. At cone 12 the former has decreased, whilst the number of bright glazes has increased. A few of the glazes were "bubbly" at the higher temperatures, particularly when fired to cones 14 and 16. The value of the work is enhanced by the author's method of illustrating his conclusions graphically. His charts show that the deformation eutectic axis commences at a composition of approximately 20% clay, 10% flint, and 70% fluxes, and lies between the high "gloss" axis and partially within the actual crazing area. Previous experimenters had reported glazes which crazed when over-fired, and it is interesting to find additional confirmation of this in the paper under review.

A writer[29] reports the possibility of using bog iron ore as a glaze for roofing tiles, and further suggests that, with slight modifications, the material can be used as an engobe for facing bricks and terracotta.

A. Bigot[30] calls attention to a peculiar defect occasionally met with in once-fired coarse pottery. Under certain conditions the glazed surface appears to be dull and immature. He indicates that, when this occurs, the clay contains abnormal quantities of a dark material which has a distinctly sulphurous odour; he assumes that the trouble is due to the presence of basic sulphates, formed by the reaction between the sulphurous fumes given off by combustion of the dark material and the basic oxides in the glaze. He argues that if this were the case, the carbonaceous and sulphurous matter must be burned out at temperatures below that at which reaction with the glaze constituents could take place. By a critical study of the time-temperature curves he found that

[28] *Ibid.*, 1921, **4**, 718; *J.*, 1921, 891A.

[29] *Deuts. Töp. Zieg. Zeit.*, 1919, **50**, 325.

[30] *Rev. Mat. Const. Pub.*, 1921, **137**, 20.

slower firing in the initial stages invariably gave better results, thus showing that his original supposition was justified.

S. Suzie [31] has produced a bright red enamel by carefully heating to 700° C. mixtures containing 80–90% of cadmium sulphide and 20–10% of selenium. He suggests that a sulphide, which may be represented by the formula Cd_3SeS_2, is formed during the process.

Earlier work by Koenig is referred to in a note on the application of the leucoscope to pyrometry, by J. G. Priest,[32] who describes an instrument which, he claims, is capable of measuring the intensity of colour, particularly the red series, and thus might be used as an optical pyrometer. The personal factor, however, already a drawback to certain optical pyrometers, is still present in an instrument such as that described.

It is generally recognised that thorough mixing of the clay and grog is essential to the production of satisfactory saggars; the method adopted by F. K. Pence[33] in the preparation of saggar mixtures is therefore worthy of an exhaustive trial. In this process the required amounts of the two materials are weighed out in a dry condition, fed into a rotary mixer similar to those used for concrete, suitable quantities of water being added after mixing, and the whole mass then well pugged. It may here be noted that W. K. Brownlee and A. F. Gorton [34] condemn the use of this type of mixer, since there is a tendency, in their opinion, for the materials to become separated by the rolling motion.

G. Simcoe has previously [35] published several important papers on the production of saggars. His latest work[35] has been on a somewhat wider basis, inasmuch as it takes the form of a review of the saggar situation in America. A very comprehensive questionnaire was issued to about thirty factories engaged in various branches of the ceramic industry, and the published data may therefore be said to be representative of modern American practice. A broad view of the subject has been taken, so that the personal factor is not strongly emphasised. The writer notes that a number of firms are introducing from 10 to 30% of carborundum in the saggar mixture. It is reported that increased tensile strength is obtained if a portion of the added water is replaced by a smaller quantity of sodium silicate. It is claimed that jaw crushing gives a better quality of grog than pan grinding, but it may be pointed out that the particular factory which furnished this information does not include any fine grades in its saggar mixtures,

[31] *J. Chem. Ind. Japan*, 1921, **24**, 252; *J.*, 1921, 390A.
[32] *J. Opt. Soc. Amer.*, 1920, **4**, 448.
[33] *J. Amer. Ceram. Soc.*, 1921, **4**, 459; *J.*, 1921, 771A.
[34] *Ibid.*, 1921, **4**, 97.
[35] *Ibid.*, 1921, **4**. 393.

so that the improvement may be due to increased output of the particular sizes required, rather than to any alteration in the shape of the grog particles. Re-pugging is considered to be indispensable by the majority of the firms contributing to the review. Cast saggars are now in use, with and without carborundum, and are apparently giving every satisfaction. A chart showing the relative costs of saggars containing carborundum as compared with the fireclay-grog type is instructive, for, assuming that the life of the former type is three times that of the latter, it indicates clearly that in America the carborundum saggar is decidedly the cheaper. Summarising, the author suggests that more information is needed before the data can be properly correlated. He is particularly desirous of securing more detailed statistics relating to carborundum, and points out that factors other than the low coefficient of expansion must operate. Simcoe considers that, in view of the increased capital outlay, greater attention will be paid to the mixing, making, and drying and firing processes, and thus some of the resulting benefits may not be due solely to any inherent qualities of the mixture. It may be suggested, however, that experiments with super-refractories appear to indicate that carborundum saggars would have a high mechanical strength and also be very resistant to crushing strains at high temperatures. Economies in fuel consumption may also be reasonably expected, considering the low specific heat and high thermal conductivity of this material.

Reference is made to carborundum in B. J. Moore's valuable contribution, "Notes on Saggars."[36] This report is interesting, inasmuch as the author discards fireclay entirely, using china clay as the refractory material, and ball clay as the binding medium. (Incidentally, it may be noted that M. K. Hornung,[37] among others, has reported the use of similar clays for this purpose.) At temperatures approaching cone 9, Moore uses a mixture containing three parts of china clay to one of ball clay; for lower temperatures a larger proportion of the binding clay is necessary. Various proportions of carborundum or fused quartz were mixed with the clay base, these materials thus replacing the normal grog. The plant available for the preparation of the mixture was admittedly inefficient; the author considers that better results could be obtained with correctly designed methods of preparation. Large batches of both types were prepared, but owing to the slightly reducing action experienced in the china biscuit oven, together with the exceptionally high capital outlay on carborundum, his latest trials were limited to mixtures of fused quartz and clay. Sound saggars containing fused quartz, which had been fired twenty times to cone 9, were exhibited by the author, while others, used to

[36] *Trans. Ceram. Soc.*, 1920, **20**, 93; *J.*, 1921, 771A.
[37] *J. Amer. Ceram. Soc.*, 1920, **3**, 69; *J.*, 1920, 369A.

cone 3 for 30—40 firings, were in an equally good condition. Special attention was drawn to the general cleanliness and freedom from slag spots, which in ordinary practice are liable to contaminate the bedding material. A marked difference was noticed when the quartz saggars were struck with a hard object; they gave a "dead" ring as compared with those of the fireclay-grog type, a characteristic which would be distrusted in general practice, but the author states that his best results were obtained with such saggars.

In the discussion which followed, it was stated by C. Bailey and H. E. Wood that the results of their experience were not in accordance with those obtained by Moore; they considered that carborundum was superior to fused quartz, since their saggars containing the latter material became brittle, and had to be discarded after comparatively few firings. Later, it was argued that this physical change was due to inversions in the quartz, and that the results were analogous to those reported by various workers on the deterioration of quartz pyrometer tubes. When further data become available, it may perhaps be possible to discover the cause of the discrepancies in the two points of view; in any case, the author is to be congratulated upon awakening interest in a subject of great importance.

Coming to enamelling, mention must be made of a reading list with reference to vitreous enamelling on iron and steel, compiled by C. J. West.[38] This list should be of great service bibliographically.

An account of a new spraying method has made its appearance,[39] which, if successful, will mark a great advance in enamelling processes. In this system, which appears to be a modification of the "Schoop," the powdered enamel is drawn from a container by means of dry compressed air or oxygen. The patent sprayer has two jets, one of which conveys the powder, the other combustible gases, such as hydrogen, acetylene, coal-gas, etc. The enamel is fused directly on to the metal, the intermediate ground coat being dispensed with. It is claimed that enamelled surfaces prepared by this process possess greater elasticity than those produced in the ordinary way.

B. T. Sweeley[40] reports the results of his work on arsenic enamels for copper. The object of the research was to produce an enamelled surface similar to watch dials, but in a thicker layer. The author states that, when the wet slushing method has to be used, a lead-free ground coat is indispensable, since lead enamels will attack copper. In all his experiments the dry dusting process was adopted. Using base enamels corresponding to the formula:—

[38] *Ibid.*, 1921, **4**, 47.

[39] *Sprechsaal*, 1921, **54**, 490.

[40] *J. Amer. Ceram. Soc.*, 1921, **4**, 350; *J.*, 1921, 511A.

$0\cdot40K_2O$, $0\cdot10Na_2O$, $0\cdot50PbO$, $0\cdot10Al_2O_3$, $0\cdot15B_2O_3$, $1\cdot80$–$2\cdot20$ SiO_2, it was found that the trials fractured with each additional increment of SiO_2. Other series were tried, in which B_2O_3 was the variable factor. When present in molecular proportions greater than 0·2 this compound produces matt surfaces. By decreasing the PbO and increasing the K_2O content, the opacity was lowered and the enamel became completely soluble in water. There is need for further reliable data relating to enamels containing arsenic or bismuth, since for certain purposes they possess very desirable qualities, but owing to defects occurring during their manufacture, and. in the case of bismuth, arising whilst in use, their field is limited.

Fish scaling, a defect common to enamelled ware, has been the subject of a research by R. R. Danielson and W. H. Souder.[41] They studied the effect of the various fluxes used in commercial enamels, and state that cryolite and soda are superior to fluorspar, whilst boric acid gives a poor result. Recognising that the composition of an enamel may be only of secondary importance, the authors extended their investigations to a study of the relative coefficient of expansion of the stock and enamels, and the presence of strains etc., in the metals used. They state that mechanical treatment of the stock, followed by careful annealing, will cure the defect. This contribution is a valuable one, the investigations covered a wide field, and the data are carefully tabulated. The facts emphasised are that, though the effect of coefficient of expansion is important, other factors, *e.g.*, elasticity and tensile strength of enamel, presence of strains between stock and enamel, are to be taken into account. It is interesting to note the analogies in their methods and conclusions with those of ceramists who have studied the causes of crazing and peeling of pottery glazes.

The relation of composition of enamels to solubility in acids is dealt with by H. F. Staley.[42] He does not consider that the alteration in weight of an enamel after immersion in acid, is a criterion of its relative solubility, since in some cases an enamel may take up radicles from the acid, and increase in weight, though actually it has undergone disintegration. The author states that compounds vary considerably in their behaviour as regards giving to an enamel acid-resisting properties, and arranges them in the following order of effectiveness :—Al_2O_3, Na_3AlF_6 (cryolite), Na_2O, PbO, BaO. The effect of ZrO_2 and TiO_2 when substituted for small amounts of SiO_2 was investigated; ZrO_2 was found to be the more effective, but this improvement in acid-resisting property is offset by a tendency to produce excessive chipping and scaling.

[41] *Ibid.*, 1921, **4**, 620; *J.*, 1921 891A.

[42] *Ibid.*, 1921, **4**, 703; *J.* 1921, 892A.

Zirconia is receiving close attention by enamellers interested in opacifiers other than tin oxide. In several instances brought to the writer's notice base enamels similar to those found to be satisfactory when tin oxide is introduced have been used. This procedure is, in many cases, unsound, since modifications will have to be made if the maximum opacity and whiteness is to be obtained from a minimum amount of zirconia.

Building Materials.

The general properties of a large number of early English mortars of the Roman period have been investigated by W. J. Dibdin.[43] He found that the ancient mortars have a higher percentage of lime and larger-sized aggregates than the modern types. This report is more interesting than informative.

H. H. Sasche [44] reports the preparation of a new anhydrite mortar; he claims that with fine grinding a very hard, cementy material is produced, particularly when 1–3% of lime or Portland cement is added.

In preparing a plastic gypsum plaster, according to W. E. Emley [45] the grinding is carried out without the evolution of water. This method is said to give a compound which sets harder than ordinary gypsum. The plasticity of the product depends upon the duration and speed of grinding, the best results being obtained when the material leaves the mill with a water content of 6·2%. T. W. Cappon,[46] in a criticism of Emley's work, points out that the effects of fine grinding were already well-known and understood; and he makes reference to a previous paper by himself on the same subject. Grinding, after calcination, he says, is strictly limited by economical factors. He considers that "mass action" is enhanced by fine grinding. Furthermore, he asserts that though water is ground out by excessively fine grinding, the 6·2% of water, mentioned by Emley, is not necessarily the result of special grinding, but is a figure depending on the degree of calcination.

A suggestion is put forward by W. E. Emley and C. F. Faxon [47] for the preparation of a coloured wall plaster. Wood fibre, soaked in aniline dyes, is incorporated with a gypsum plaster, which is then applied in the usual way. The setting can be retarded by the addition of lime and clay.

A new "wet" process for the preparation of lime is indicated by N. C. Rockwood.[48] In the presence of water vapour, limestone dissociates at a lower temperature than it does in a dry atmos-

[43] *Trans. Faraday Soc.*, 1921, **17**.
[44] *Tonind. Zeit.*, 1920, **44**, 1017.
[45] *Chem. and Met. Eng.*, 1921, **24**, 740; *J.*, 1921, 849A.
[46] *Rock Products*, 1921, **24**, 19, 49.
[47] *U.S. Bureau of Standards*, *Tech. Paper* 181.
[48] *Rock Products*, 1921, **24**, 19.

phere. Steam combines with carbon dioxide to form hot carbonic acid, which rapidly disintegrates the stone, and calcium bicarbonate is produced, which has a greater volume than the underlying stone; consequently strains are set up, sufficient to disintegrate the mass. Herzfeld's experiments on the effect of superheated steam on lime burning are referred to. The fact that lime, burned with wood, hydrates very readily appears to be due to similar causes. Water-gas also acts in an analogous manner. It may be questioned, however, whether calcium bicarbonate would be present for a sufficiently lengthy period to act as suggested.

Attention is drawn by the U.S. Bureau of Standards [49] to the corrosive effect of cement retarders containing chlorine compounds, *e.g.*, calcium chloride, on steel or galvanised reinforcements. Laboratory experiments conducted by the National Lime Association emphasise the fact (previously noted as the result of field trials) that an addition of 5% of hydrated lime to motrar and concrete mixes prevents the corrosion of the metallic reinforcements.

Laboratory tests carried out by R. Grün [50] prove that when alkaline concretes are worked sufficiently to reduce porosity to a minimum the liability to rusting of the steel reinforcements is considerably diminished. The author observes that the reinforcements remain unaffected in concrete compounded from slag cement, Portland and iron-Portland cement.

The effect of storage on the properties of cements has been studied by D. A. Abrams.[51] A number of concrete cements were stored under varying conditions—in the open and under cover—for certain periods. Compression tests showed that exposure under an open shed had a very marked influence; after one year the material had retained only 61% of its original strength, this being reduced to 40% after exposure for a further twelve months.

P. H. Bates and R. N. Young [52] have given their attention to plastic magnesia cements. They covered the whole field rather exhaustively and collected a mass of data, many of which, however, are inconclusive. The material used, which was the crystalline magnesite from Washington, was sieved into three grades before calcination, each grade being used separately. Whilst the differences between the results of the tests for the various grades were not great, the finest material, through a 60's lawn, gave slightly better results than the coarser sizes. The authors state that great economies in the use of magnesium cements, calcined at low temperatures, may be effected by using the more highly-concentrated solutions of magnesium chloride; increased quantities

[49] *Cement and Eng. News*, 1921, **33**, 21.
[50] *Stahl u. Eisen*, 1921, **40**, 577; *J.*, 1921, 472A
[51] *Cement and Eng. News*, 1921, **33**, 29.
[52] *J. Amer. Ceram. Soc.*, 1921, **4**, 570; *J.*, 1921, 848A.

of a weaker solution will not lead to the same result, thus each material should be tested with various strengths of solution above and below the usual 23° B. if the best results are to be obtained.

Discussing tentative tests of oxychloride cements, M. Y. Seaton[53] suggests that change in volume, time of setting, and permanence are of greater importance than compression or tensile strength determinations. With regard to the action of lime on magnesium oxychloride cements, the same writer,[54] in conjunction with C. R. Hill and L. C. Stewart, describes a method of determining the amount of harmful or "active" lime in the compounds used. They conclude, however, that, at present, physical tests of oxychloride cements are the only safe criteria of quality. With regard to the action of tannic acid on concrete, D. A. Abrams[55] has stated that this compound reduces the tensile strength, the effect being very marked on lean concrete with large aggregates. It was noted, however, that the decrease was not so marked in the specimens that had been stored from one to two years.

The effect of hydrated lime and other powdered admixtures in concrete has been studied in some detail by D. A. Abrams.[56] His chief conclusions are that: the addition of hydrated lime to concrete reduces the compressive strength to an extent almost proportional to the amount added; for the usual concrete mixtures the average reduction in strength is 0·59% for each 1% of hydrated lime added, whilst under the same conditions the addition of 1% of cement increases the strength of the concrete by about 1%; with a constant quantity of mixing water in 1 : 4 and 1 : 5 mixes, hydrated lime shows an increase in strength of 0·61% for each 1% added, as compared with 2·37% for each 1% of Portland cement; and under identical conditions the addition of either hydrated lime or Portland cement up to 33% produces essentially the same effect on the "flow" of concrete.

A ferriferous agglomerant, capable of replacing either iron-Portland or ordinary Portland cement, is described by F. Ferrari.[57] Impure limestone, clay, sand, and ferric oxide—the latter obtained by burning pyrites—are employed to produce a cement that is said to be stable towards chlorides and sulphates, and to contain a high percentage of hydraulites. If the high basicity of the cement be modified by the addition of puzzuolanic substances, the resultant product is absolutely impermeable and possesses a high mechanical strength as compared with ordinary Portland cement.

[53] *Chem. and Met. Eng.*, 1921, **25**, 233; *J.*, 1921, 659A.

[54] *Ibid.*, 1921, **25**, 270; *J.*, 1921, 659A.

[55] *Proc. Amer. Soc. Testing Mat.*, 1920, **20**, [1]; *Bull.* 7, *Structural Materials Res. Lab., Lewis Inst., Chicago*; *J.*, 1921, 180A.

[56] *Ibid.*, *Bull.* 8; *J.*, 1921, 814A.

[57] *Giorn. Chim. Ind. Appl.*, 1921, **3**, 53; *J.*, 1921, 260A.

Ferro-concrete is proposed as a suitable material for the construction of by-product coke-oven plants,[58] particularly in the construction of washeries, coal bunkers, and foundations to the benches. It might also be employed as a foundation for the sulphate-house floor, if covered with acid-resisting tiles. The material would undoubtedly be less liable to the corrosive action of gases etc., but here, as in the case of all large buildings constructed of this material, it is important to see that the structure is well designed in the first place, since subsequent alterations are extremely difficult to carry out.

J. E. Pearson,[59] in his study of the cracking of stucco, has supplied much-needed data concerning the effect of non-porous forms on the setting and surface shrinkage of concrete. Careful observations were made on concrete mixes run into (*a*) wooden forms, and (*b*) plaster of Paris forms. It was found that the resulting partial absorption of moisture from the mixtures in the latter type reduced the contraction very considerably, thus avoiding the production of map-crazing in stucco work.

Interesting data relating to street-paving with sand-lime bricks are reported by H. Jolig.[60] A careful examination of bricks that had been used in a road subjected to abnormally heavy vehicular traffic for ten years, showed that they were still in excellent condition, and had only worn down to the extent of 10–20 mm.

According to E. C. Blanc and K. Gerson,[61] artificial stone blocks are made from bauxite or residues from the manufacture of aluminium, together with fat or hydraulic lime, by methods similar to those employed in the manufacture of sand-lime bricks. Another method for the production of building blocks, suggested by A. Wilkinson,[62] consists in lining the moulds with a granular material, such as sand, in which the hard objects (pieces of stone, slag, brick, etc.) are partly embedded before the binder is run in.

For the manufacture of light plaster of Paris bricks,[63] ordinary gypsum is used as a binder with the addition of coal ash, sawdust, pumice, sand, etc., the proportions depending upon the quality of the materials. Satisfactory bricks were produced by using 1 part of plaster, 3 parts of ash, and 1·5 parts of water. The crushing strength of the finished article is stated to be 30 kg. per sq. cm.

Considerable sums of money have been expended during the last decade on experiments designed to utilise the spent product remain-

[58] *Gas World*, Aug. 6, 1921, *Coking Sect.*, 14.

[59] *Cement and Eng. News*, 1921, **33**, 27.

[60] *Tonind. Zeit.*, 1920, **44**, 703.

[61] G.P. 327,906; *J.*, 1921, 181A.

[62] E.P. 163,512.

[63] *Tonind. Zeit.*, 1920, **44**, 1259.

ing from the distillation of the Scottish oil shales. According to a report,[64] the problem has now been solved satisfactorily. By slight modifications of the sand-lime brick process first-class building bricks are being produced. Special attention is given to the securing of perfect homogeneity of the shale-lime mixture previous to making into bricks. This departure is of great importance, since huge supplies of raw materials are available in positions eminently suitable for economical layout and cheap transport facilities.

With the object of saving fuel, much attention has been given on the Continent to the possibility of utilising unfired bricks for building purposes.[65] Raw bricks have been tested for resistance to compression, and it was found that machine-made bricks resist crushing strains much better than the hand-made variety.

The use of silica in wood fillers is reported by F. A. Ingall.[66] The form of silica which is said to be an ideal material for this purpose is quartz; it is free from colour, inert, and shows no tendency to react with other constituents. Its refractive index is near to that of paint vehicles, whilst its crystalline condition gives it a small specific surface when powdered.

A "cold" glaze for surfaces such as concrete, stone, brickwork, etc. is reported.[67] The patentee claims that inferior surfaces may be sprayed with the mixture in order to give them an impervious coat, and that the glaze can be produced in any desired tint. If the claims made by the patentee are sound, the process would appear to offer great possibilities.

S. Miall[68] contributes an interesting report on occupational diseases. Medical testimony supports the view that habitual headaches, kidney trouble, and gout may be caused by the inhalation of turpentine vapours, and the author states that many cases diagnosed as lead poisoning are really due to this cause. The dust usually produced when rubbing down old painted surfaces may be obviated if the abrasive pad is moistened with a mineral oil. Attention is called to the modern lead substitutes, such as titanium, antimony, etc. It is pointed out that their toxic effects will be almost as injurious as those of the lead compounds they are intended to replace.

Ceramic Firing Technique.

As is pointed out on p. 228, much attention has been devoted during the past year to firing methods in the ceramic industry,

[64] *British Clayworker*, 1921, **30**, 224.
[65] *Rev. Mat. Constr. Trav. Pub.*, 1921, **136**, 12B (March 12).
[66] *Rock Products*, 1921, **24**, [5], 40.
[67] E.P. 154,236: *J.*, 1921, 47A.
[68] *J.*, 1921, 140R.

and to fuel economy generally. It is therefore deemed advisable to devote a special sub-section to this subject, embracing the firing of all kinds of clay products, including refractories.

In his Presidential address to the Refractory Materials Section of the Ceramic Society, Lt.-Col. C. W. Thomas draws special attention to the importance of industrial research, including, among other things, the need for a careful study of the economic application of fuel and of the closely-related question of the most efficient design for kilns and furnaces.

A problem of some difficulty, which still awaits complete solution, viz., the mechanical handling of bricks during the setting and drawing operations, has been tackled with some success by R. C. Penfield.[69] The machine which he describes is used in connexion with a scove kiln. From 750 to 1000 bricks are placed at one operation; the uniform spacing achieved assists in attaining a successful burn. Drawing is effected by the same machine, the bricks being picked up in the same order and placed on trucks. The greatest drawback attending the use of scove kilns, is the excessive labour costs, and in this connexion the invention is undoubtedly an important one, but it would appear to be applicable only to very large kilns.

In a detailed report W. W. Dickinson[70] describes a scove kiln which possesses unusual features. The kiln is situated in a large shed, into which is fitted a powerful travelling crane. Two brick walls or necks are built up, vitrifiable cement being used between each course, so that a monolithic structure results after the first firing. Green bricks are built up in the usual manner (but without casing), the fired walls being then removed *en bloc* into position, ready for the firing operation. When this is completed, they are transported by the crane and placed into position elsewhere, ready for the firing of another section. This system must represent a considerable saving in labour and fuel, whilst the burn will be more uniform, since cold air leakages will be considerably reduced.

In another contribution to the subject of scove kilns, T. H. Lambert[71] deals with the "Chicago method" of burning bricks. In this process, a portion of the fuel is incorporated in the clay mixture, and the bricks are set into position by the Penfield machine. Air, and oil atomised by steam, are blown into the "live" holes until "settle" commences—this usually after 18 hours. At this point a temperature of 1900° F. is reached at seven courses, 480° F. at 21 courses, and 210° F. at 42 courses from the base. The oil is then shut off, only air and steam being injected for the next 26 hours. At the expiration of this time the temperatures are

[69] *National Brick Manufrs. Assoc. Report*, 1921, p. 113.

[70] *Brick and Clay Rec.*, 1921, **59**, 29.

[71] *Clayworker*, 1921, **12**, 244.

550°, 1380°, and 1750° F., respectively. For the final six hours air alone is blown in, and when the kiln is finished the respective temperatures are usually 400°, 1100°, and 2000° F. Excellent diagrams accompany the paper, and from these, time-temperature and distance-temperature charts can be readily constructed. If Kentish clays are amenable to such treatment it ought to be possible, by a combination of the foregoing processes, to abolish some of the antiquated and wasteful operations at present in vogue for the production of London stock bricks. It is, indeed, remarkable how these out-of-date methods still persist in Britain, despite the wealth of reliable information available concerning the specialised mass-production of common bricks in other countries.

In connexion with the avoidance of unnecessary heat losses, one writer[72] notes that it is important for exposed kiln crowns to be rendered thoroughly waterproof. Layers of cinders, grog, clay, and, finally, asbestos sheets should be applied to the crown, to serve the double purpose of preventing ingress of water, and at the same time, excessive radiation losses during the firing operation.

In a symposium on gas-firing conducted by the Ceramic Society, C. W. Spiers[73] gave some interesting details of his experience with an intermittent kiln encased in ferro-concrete. He claimed that considerable economy in fuel is effected by the prevention of air leakages in such structures. A. Bigot[74] had already advocated a similar procedure for continuous tunnel kilns.

According to a report by K. Rieke,[75] twenty-six firms in Germany are utilising waste heat from the cooling ovens in their making and drying operations. It should be noted that in practically all new continuous ovens, arrangements are made to use waste heat in a similar manner.

The capital outlay involved in the erection of large continuous ovens has led to extensive research on the possibilities of grouping existing periodic kilns, so as to enable them to be worked in a semi-continuous manner. The design of ceramic works, however, does not usually allow even a limited grouping to be effected economically, but several promising methods are indicated in recent patent literature.

In intermittent ovens little attention is paid to the question of the transfer of heat, since in the relatively large heated spaces filled with ware it is difficult to decide whether conduction, radiation, or convection is the most important factor. But in the case of certain continuous firing systems, *e.g.*, the Dressler, it is claimed

[72] *Rev. Mat. Constr. Trav. Pub.*, 1921, **136**, 12B.
[73] *Trans. Ceram. Soc.*, 1921, **20**, 36.
[74] *Ibid.*, 1919, **18**, 285.
[75] *Ber. deuts. keram. Ges.*, 1920, **1**, 36.

that the heating is effected mainly by convection currents, so that the research reported by A. H. Davis[76] in this connexion should be of considerable value. He shows conclusively that a direct relation exists between the geometrical form of the surface of a heated object and the convection currents set up.

C. B. Harrop[77] publishes data relating to two direct-fired continuous tunnel ovens, one of which is firing biscuit to cone 10 and the other glost to cone 6. They are placed end to end in one shed, the total length of the two kilns being approximately 200 yards. Relatively small mouths with specially designed coking tables are used, the average thickness of the fuel bed being 15 in. The tunnel proper is wider at the base than at the top ; this construction is considered to equalise the temperature inside the tunnel. Hydraulic power is used to move the trucks. The value of Harrop's contribution is enhanced by the fact that it enables a comparison to be made between direct and gas-firing as applied to modern tunnel kilns. His data concerning the power required to move the trucks will, no doubt, be appreciated by kiln designers.

Despite the rapid advance in the application of gaseous firing systems to the ceramic industry, many problems still remain unsolved. It is true that certain kiln designers and experts have publicly stated that any type of clay product can be successfully dealt with. Other technical experts, however, recognise the limitations of the newer systems.

Many interesting points were raised at the meetings of the Smoke and Noxious Vapours Commission at Stoke-on-Trent. B. Moore[78] admitted in his evidence before the Commission that, in certain branches of ceramics, gaseous fired ovens and kilns were giving great satisfaction, but he stated that, up to the present, extended trials in gas firing had not proved successful in the production of bone china ; a further statement that, in specified firing operations, a certain amount of "necessary" smoke was produced, appears to have perturbed the members of the Commission, but there can be no doubt that, in the production of certain goods, the necessity of a deposition of solid carbon within the pores of the ware can scarcely be disputed. Moore's observations are valuable, since many ceramists and kiln designers, though well aware of the fact that, for certain goods, a reducing atmosphere is necessary during certain stages of the firing operations, do not differentiate between an atmosphere deficient in oxygen, and one in which the reducing conditions are mainly due to the presence of solid carbonaceous matter. C. Bailey[79] intimated that a sub-committee had been

[76] *Phil. Mag.*, 1920, **40**, 692.
[77] *J. Amer. Ceram. Soc.*, 1921, **4**, 673.
[78] *Pottery Gazette*, 1921, **46**, 93.
[79] *Ibid.*, 1921, **46**, 96.

appointed by the British Pottery Manufacturers' Federation to make an extended and scientific investigation into the merits (or otherwise) of continuous gas-fired ovens and kilns, and that eminent gas experts who had gained experience of gaseous systems in other industries had been co-opted on the committee. Bailey rightly appreciates the difficulties confronting the Commission, particularly as regards the application of gas firing to the smaller manufactories, whose present output does not exceed two biscuit and two glost ovens (or even less) per week.

In his introduction to the symposium on gas-firing [80] previously referred to, E. W. Smith discusses at length the suitability of various industrial gases for the ceramic industry, and emphasises the necessity of a regular supply at uniform pressure, specific gravity, and calorific value. He considers that the economical application of town gas is limited to a few specific cases, though the adoption of surface combustion principles would probably widen its scope. Smith claims that producer gas is eminently suitable for ceramic purposes ; its relative cost per thermal unit is lower than that of either blue-water gas or town gas. He also mentions that, in choosing a fuel for a producer, it is advisable to work with one type only, rather than with a mixture, though in several instances the present writer has noted better results from a combination of 90% coke and 10% bituminous coal than from coke alone.

E. M. Myers[81] is of the opinion that blast-furnace and coke-oven gases, particularly the latter, will become of great industrial importance, apart from their use in metallurgical operations, and will eventually be available for distribution in bulk in certain areas.

In view of the rapid strides the various gas-firing systems are making, the exhaustive summary of the causes of thermal losses in gas producers by N. E. Rambush[82] is a welcome contribution to our knowledge of the subject. He attempts to correlate laboratory results with works practice, and puts forward simplified calculations for estimating the thermal efficiency. His data, showing the relationship between the thickness of the fuel bed, the rate of combustion, and the temperature of the issuing gases, are distinctly useful. The paper is of great interest and value to technical men.

The advantages and disadvantages of the application of producer gas to periodic muffle kilns are discussed in a lengthy paper by F. B. Ortmann.[83] On the basis of his observations, he states that there is little or no fuel economy to be gained by the substitution of gas for solid fuel. During his remarks on the working of a coal-fired

[80] *Trans. Ceram. Soc.*, 1921, **20**, 20.

[81] *Ibid.*, 1921, **20**, 24.

[82] *J.*, 1921, 129T.

[83] *J. Amer. Ceram. Soc.*, 1921, **4**, 669.

continuous chamber oven, C. W. Thomas[84] quoted fuel costs which are comparable to modern gas-fired kilns. His figures, in fact, are lower than those for many gas-fired installations producing similar refractory goods. He indicates, however, that the advantages of the centralisation of the fuel supply in lowering labour costs, and ensuring additional cleanliness, together with the ease of control, are such that the introduction of the gas-fired system would repay the extra capital outlay involved.

C. J. Hudson[85] has studied the thermal efficiency of a Dressler kiln, burning natural gases, used for firing glasshouse refractories. In general, the constructional details were similar to those of other Dressler ovens, but special arrangements had been made to enable accurate temperature measurements to be taken, no less than 17 pyrometers having been installed for this purpose. Cross-sectional heat distribution was largely governed by the method of placing the goods on the trucks. The latter occupy eight days in passing through the kiln, the refractories varying in weight from a few pounds up to a ton. For similar pieces a minimum of 21 days would be required in an intermittent kiln. If, in a large periodic kiln, the rise in temperature in the portion adjacent to the firing boxes is such as not to injure the goods in the immediate vicinity, then the firing rate in the interior of the kiln will necessarily be very slow. When dealing with relatively large units at non-uniform temperatures, the firing operations are conducted with extreme caution to get satisfactory results. The paper is worthy of study, in spite of the mass of data on Dressler kilns already published.

J. H. Marlow has patented another modification of his gas-fired tunnel kiln. According to the details given of the graduated burner,[86] a better heating gradient should be obtained. The patentee claims that the kiln has been fired to 1600° C., and that such elevated temperatures are well within its range. It should be noted that the only published data referring to runs over a reasonably long period relate to the firing of goods requiring much lower temperatures.

According to E. P. Benjamin,[87] a tunnel oven is constructed with external combustion chambers containing chequered brickwork, hot blast stoves with the necessary reversing valves being also incorporated in the system. This patent appears to be an interesting application to ceramic practice of firing systems usually associated with metallurgical operations.

[84] *Trans. Ceram. Soc.*, 1921, **20**, 34.
[85] *J. Amer. Ceram. Soc.*, 1921, **4**, 751.
[86] E.P. 155,190; *J.*, 1921, 82A.
[87] E.P. 140,578; *J.*, 1920, 356A.

C. H. Zwermann's plant [88] consists of adjacent twin tunnels operating in opposite directions. Part of the heat is withdrawn from the cooling zone of one tunnel and passed into the heating zone of the other. The burners are situated near the roof of the tunnel, the hot gases being drawn into flues arranged in the bottom of the tunnel structure.

H. Barkby [89] describes a "Faugeron" kiln that is working successfully in Czecho-Slovakia for the production of hard porcelain. In general the construction is similar to that of the original types, but modifications have been introduced with the object of ensuring the reversal of the flow of gases through the system -- the characteristic feature of all true Faugeron kilns.

During 1921 several tunnel ovens distinct from the Dressler type have been put into operation for the firing of porcelain, whiteware, stoneware, tiles, etc., and though there are no data published there is no doubt that in most cases they are working satisfactorily. A pleasing feature in connexion with tunnel ovens is the readiness with which the interested parties will furnish any desired information relating to constructional details, working costs, etc.; this procedure will naturally lead to increased favour and confidence in the tunnel systems.

For a considerable number of years the "Dunnachie" gas-fired chamber oven has been used successfully for firing refractory goods, and J. Dunnachie [90] claims that the most complete combustion may be expected from kilns in which the combustible gases and secondary air are fed directly among the goods, the chamber itself acting as a combustion chamber, thus ensuring maximum fuel economy without loss of space due to flash walls etc.

Summarising his experience with gas-fired chamber ovens, Richmond [91] states that the use of "perforated candles" is an ideal method of getting uniform distribution of temperature.

Of recent years considerable attention has been devoted to the evolution of gas-fired chamber ovens for the production of general whiteware, enamelled fire-clay, glazed bricks, and sanitary goods. The underlying principles of the construction of such chamber ovens already erected are similar to those used in the refractories and face brick industry, with, of course, the modifications found to be necessary to meet specific conditions. A number of the "Shaw" and "Thompson" ovens are now in use, whilst others designed by expert ceramic engineers are nearing completion. It is to be desired that sufficient data relating to these latest types of chamber ovens may soon be available; their efficiency can then be

[88] E.P. 140,740; *cf. J.*, 1919, 636A.
[89] *Pottery Gazette*, 1922, **47**, 77.
[90] *Trans. Ceram. Soc.*, 1921, **20**, 27.
[91] *Ibid.*, 1921, **20**, 30.

compared with the tunnel ovens now used for the firing of similar goods.

One of the chief drawbacks to the more rapid introduction of continuous kilns on existing works is the lack of ground space. A report[92] on a vertical oil-fired continuous oven is, therefore, of interest. According to the writer, bricks can be passed through the kiln in 14 hours, but the actual data published do not warrant definite conclusions. A vertical gas-fired continuous kiln, suitable for whiteware products, is described by E. F. Chaudiere.[93] An oven has been built for experimental and demonstration purposes; the results of the working of this system will be awaited with keen interest, particularly by the smaller manufacturing concerns. It may be noted, however, that the mechanical difficulties associated with ovens or kilns of this type are likely to be greater than those met with in horizontal tunnels.

Further progress has been made in the application of powdered fuel to various burning processes, notably in rotary cement clinker kilns. The experiments described recently[94] will be followed with interest by brick manufacturers, since it is claimed that, by a modification of the plant therein described, the irregular heating and local slagging of bricks experienced in the initial experiments will be obviated.

Colloidal fuel, mainly an emulsion of heavy mineral oils and finely-divided coal, is being tested on a commercial scale for the firing of refractories. The results will be awaited with interest.

The account of a twin tunnel oven designed to burn fuel oil, given by P. J. Woolf,[95] will, no doubt, receive the close attention of ceramists. The author, however, admitted, during the discussion, that, up to the present, the kiln had only been fired by town gas. In one respect this is advantageous, for it has been suggested that town gas may be economically employed in modern kilns, so that, if the running costs of gas and fuel oil on the same kiln are published, direct comparison will be possible. Even in cases where fuel oil has to be imported, its use will doubtless become popular in certain branches of the ceramic industry, *e.g.*, in fritt kilns etc.

A number of gas furnaces embodying surface combustion principles have been patented during late years, and from the available information (in most cases published by the furnace builders) it would appear that their application to specified industrial firing operations has been a success. Very high fuel economies are claimed for the system; theoretically, of course, these results are to be expected. It is to be noted, however, that the system

[92] Anon., *Brick and Clay Rec.*, 1921, **58**, 391.
[93] E.P. 137,168; *J.*, 1920, 179A.
[94] *Brick and Clay Rec.*, 1921, **59**, 586.
[95] *Pottery Gazette*, 1921, **46**, 1645.

applied to other industrial heating operations has not fulfilled the earlier promises.

In certain areas for economic reasons wood fuel is used in preference to coal for the firing of ceramic goods. It is natural, therefore, that since wood has been gasified and the resulting gases successfully used in other industries, the possibilities of applying similar principles to pottery firing are being explored.

In a discussion on gas producers with wood fuel, P. de Groote[96] claims that ceramic products can be successfully fired by means of gas generated from wood, and that the results are at least equal to those obtained with gases generated from other fuel.

The firing temperatures attainable with wood have been investigated by H. Sachse,[97] who discusses the theoretical considerations, particularly regarding the flame temperatures, after allowing for the elimination of the moisture in the wood. It is stated that the calorific value of green wood is 2160 cals., giving a theoretical flame temperature of 1500° C., which is reduced in practice to 900° C. Thus, it is argued, it would be impossible to attain to a sufficiently high temperature for glost purposes (presumably for hard porcelain).

Abnormal conditions may render it necessary to use wood fuel temporarily, and, no doubt, many experiments were made during the war period at isolated factories far removed from the coal areas. W. Lindley[98] reports the result of such a trial carried out at a pottery in Spain. In a Faugeron tunnel oven which was being fired with wood, the only structural alteration found to be necessary was an enlargement of the fire mouths. The quality of the goods was equal to that produced by coal firing, and, as was to be expected, the atmosphere in the tunnel was practically free from sulphurous fumes. It was also noted that the flues did not choke so readily. Lindley reports, however, that the saggars were adversely affected, their length of service being considerably shorter than was the case when coal firing was in use. A similar defect was noted by A. S. W. Odelberg,[99] who used two-thirds coal and one-third wood for the firing of intermittent ovens. With only this partial replacement the author states that the saggars were "scorched" and the breakage percentage considerably increased.

It was anticipated that electricity would become a serious competitor in certain industrial firing processes, where the temperatures are sufficiently low to permit the use of resister windings, and C. M. Mehling and J. W. Carpentier[100] now give details of an enamelling furnace with an internal capacity of 80 cub. ft., operating on an

[96] *Ceramique*, 1921, **24**, 1.
[97] *Tonind. Zeit.*, 1920, **44**, 709.
[98] *Trans. Ceram. Soc.*, 1921, **20**, 73.
[99] *Ibid.*, 1921, **20**, 47.
[100] *J. Amer. Ceram. Soc.*, 1921, **4**, 271.

alternating three-phase current, whilst L. Barringer[101] describes an improved form of nichrome ribbon resister furnace, with a pre-heating chamber. The figures indicate that the output is increased by 50%, with simultaneous decrease in fuel costs of 50%.

[101] *Ibid.*, 1921, 4, 461 ; *J.*, 1921, 772A.

IRON AND STEEL.

By J. H. Andrew, D.Sc.

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The state of the iron and steel industry was regarded as being bad in 1920; in the past year it has been far worse—indeed, hardly in the memory of living man has any year seen the bad trade and unemployment that has so characterised 1921.

In his presidential address to the West of Scotland Iron and Steel Institute, Mr. Andrew Gray gave the following figures relative to the production of pig iron and steel in the United Kingdom. The downward tendency of the total output is too evident to require comment:

Production of Pig Iron in the United Kingdom.

(In thousands of tons)

Month and year.	Hæmatite.	Basic.	Foundry.	Forge.	Total including alloys and other qualities.
1920—September	278·1	251·0	132·0	48 3	741·0
October	193·3	162·8	101·8	46·68	533·2
November	133 5	130·7	73·8	36·9	403·2
December	237·1	202·3	147 7	58·6	682·5
1921—January	199·2	176·2	165·5	64·9	642·1
February	171·8	97·8	127 0	41·2	463·6
March	132·0	89·4	110 3	39 8	386·0
April	16·1	7·1	25·5	9 9	60·3
May	2·8	3·4	6·9	0·5	13·6
*June	—	—	—	—	0·8
July	—	3·3	2·6	0·6	10·2
August	18·3	36·3	29·1	8·5	04·2

* No analysis, but made from two furnaces.

1020 monthly average, 667·3. 1919 monthly average, 617·0.

Production of Steel in the United Kingdom.

(In thousands of tons.)

Month and year.	O.H. furnaces.		Bessemer converter.		All other ingots and castings.	Total.
	Acid.	Basic.	Acid.	Basic.		
1920—September	329 0	463 3	44·3	35·8	12·3	884·7
October	206·9	273·0	34·5	20·9	0·0	544·3
November	188 6	250·7	30·5	25·5	9·8	505·1
December	272·4	389·6	41·6	33·3	9·7	746·6
1921—January	148·2	274·4	34·2	28·5	8·1	493·4
February	167·[illegible]	258·4	31·6	19·6	6·5	483·5
March	130·7	175·9	27·2	19·6	5·7	359·1
April	32·0	29·6	5·9	—	3·1	70·6
May	1·4	2·5	—	—	1·8	5·7
June	—	—	—	—	—	1·9
July	35·5	68·2	7·4	2·6	3·5	117·2
August	152·2	252·6	14·3	10·9	4·1	434·1
September	138·3	269·9	5·1	12·9	4·0	430·8

1920 Monthly average, 754·7. 1919 Monthly average, 658·0.

In this country the trouble has arisen chiefly on account of the high cost of production, the cost of fuel alone serving to cut us out of the world's markets. As an illustration of this, it might be related that it is cheaper to buy Belgian pig, paying freightage, than it is to buy from home producers. As the result of this, the greater part of our blast furnaces and our steel works are either completely or partially shut down.

The advent of a new year has, however, with a certain amount of reason, given rise to new hopes. One hears every week of works that have been closed for some little time opening up again, so that whereas the immediate past was bad to a degree, the near future is far from being hopeless.

The result of this slackness in the industry has not only affected the financial aspect, but has left its mark in the production of scientific and technical advances. One seeks in vain for any technical paper of merit concerning the design or operation of metallurgical plant. This being so, any review of the work of the year must necessarily concern itself almost exclusively with the more scientific publications.

Even in the field of science has this year been unfortunate; there is, indeed, a distinct atmosphere of mediocrity pervading most of the scientific works. Publications on blast furnace practice, steel furnace design, steel furnace operation, and rolling mill practice being either wanting or unworthy of consideration, we are limited almost exclusively then to the consideration of the physical properties and mechanical properties of iron and steel.

Physical Properties of Iron and Steel.

A. Portevin and V. Bernard[1] write at some length upon the coalescence in steels, meaning the coalescence of the cementite. They treat the question with regard to composition of the steel, temperature of heating, duration at the high temperature, and rate of cooling. Their results are interesting, but in many ways self-evident. Is it not natural, for instance, that with a steel in which the cementite is fully coalesced, greater time will be required for its solution upon heating above the critical point? The rate of reaction, in which is included rate of solution, will naturally bear some relation to the size of the reacting particles.

The authors attempt to measure the magnitude of the transformation point by means of the dilatometer, taking the expansion or contraction undergone by the specimen in passing through the critical point as being proportional to the magnitude of this transformation. When it is considered that this critical change represents the sum of two opposing factors, which on cooling are an expansion due to the transformation of gamma into alpha iron, and

[1] *J. Iron and Steel Inst.*, 1921, **104**, 145; *J.*, 1921, 698A.

a contraction due to the carbide, it will be realised that until we have further data upon the magnitude of these separate changes, conclusions based on such determinations are more or less useless.

One point in the paper that deserved greater consideration than these authors gave it lies in the method given for the complete spheroidisation of the cementite, which is as follows. This coalescence is, in a 0·98% carbon steel, brought about by soaking the steel at a temperature of 750° C. for 25 hours followed by a cooling to 650° C. at the rate of 5° C. per hour. In the light of the iron-carbon diagram, at a temperature of 750° C., in a steel of the stated composition, all the carbide would be in solution. The inferences to be drawn are then (1) that the depression of the Ar3 point by carbon is a purely supercooling effect, and that given sufficient time, carbide will separate out at a temperature below this change point, *i.e.*, 900° C., or (2) that the carbide at a temperature just above the eutectoid temperature is in a different state from what it is at a high temperature, a suggestion previously put forward by the writer.[2]

Mitchell[3] also refers to some extent to the divorcing of the pearlite, which reaction he illustrates by numerous photomicrographs. Mitchell does not, however, go very deeply into the question as to the methods used for bringing it about.

In neither of these papers is there any reference to a not uncommon fault in boiler plate material referred to by D. Hanson,[4] and frequently met with, in which the cementite coalesces around the grain boundaries, with the resulting development of intercrystalline weakness. If only these workers would give a little more attention to such practical problems as these their efforts would be welcomed.

In a further paper[5] A. Portevin points out that the hitherto accepted view that tungsten has a solubility of 9% in iron is incorrect, for as he shows free tungstide of iron may be present in a carbon steel containing as little as 5% tungsten.

Now, the writer has shown[6] that tungstide of iron diffuses extremely slowly, even at a comparatively high temperature, and when in a fine state of division, so that when it exists in large masses, as illustrated by Portevin's photomicrographs, or in the form of needles, an excessively long time would be required to bring about complete solution.

As the writer pointed out in his lecture, this slow rate of diffusion of the tungstide was the cause of its value in certain special steels in preventing grain growth. Until the tungsten has dissolved or

[2] *Ibid.*, 1920, **102**, 527.

[3] *J. West Scotland Iron and Steel Inst.*, 1921, **28**, [4].

[4] *Trans. Faraday Soc.*, 1921, **17**, 91 : *J.*, 1922, 104A.

[5] *J. Iron and Steel Inst.* 1921 **104** 141 ; *J.*, 1921, 737A.

[6] Lecture to Sheffield Soc. of Engineers and Metallurgists, Dec. 12, 1921.

nearly dissolved in the steel up to its saturation limit, grain development does not take place, owing to the fact that diffusion will absorb greater energy than grain growth; the former action will therefore take place in preference to the latter. This suggestion has, of course, a definite thermodynamical basis to its proof.

Dealing with the effect of tungsten, one cannot pass over without comment a remarkable statement by N. Belaiew[7] on Damascene steel, in which the author likens a Damascene blade containing 1·5% of carbon to a high-speed steel. This statement is based on the fact that in a Damascene blade the greater part of the carbide is spheroidised. It should be pointed out to Belaiew that in a high-speed steel the segregated constituent is tungstide of iron, and that, moreover, some of the best high-speed steels contain none of this compound in a free state, but are homogeneous.

An exceedingly valuable and interesting contribution to scientific metallurgy is to be found in the paper on the characteristic curves of heat treatment of steels by A. Portevin and P. Chevenard.[8] These authors, after discussing the relations between the fundamentals of heat treatment, namely, initial temperature of heating and rate of cooling, proceed to indicate, by means of very ably constructed diagrams, the effect of these two variables upon the temperature and magnitude of the critical change or changes. To cite one particular case, namely, a nickel-chrome steel, containing carbon 0·5%, nickel 2·65%, and chromium 1·60%, this steel shows, according to the initial temperature of heating, three definite critical points, one at about 600° C., which they designate as Ar′, one at about 400° C. termed Ar″, and one at about 150° C., namely, Ar‴. The magnitudes of the transformations at these particular temperatures were determined by means of the well-known Chevenard dilatometer. The decreasing magnitude of the upper point, and finally its complete depression, simultaneously with the increase in the two lower points, were noted, and measurements made of their magnitude, the results, as stated, being embodied in a simple diagram. This contribution serves as an excellent example of the application of true theory to practice, especially when, as in this case, the Brinell figures are placed in the diagram, and it makes a most useful guide to heat treatment.

Since the compositions of the special steels employed in practice are limited to a small number, it would be an excellent scheme to construct similar working diagrams to these for each particular composition. The present tendency of the French workers is to employ the dilatometer almost exclusively in the determination of the critical points in steel. No one can quarrel with this, for the method as a method is undoubtedly good. It is unfortunate,

[7] *J. Iron and Steel Inst.*, 1921, **104**, 181; *J.*, 1921, 737A.

[8] *Ibid.*, 1921, **104**, 117; *J.*, 1921, 698A.

however, that so little attention seems to be given to English work on similar lines. For instance, Portevin and Chevenard,[9] in discussing the dilatation curves for an eutectoid steel, remark upon the period of dilatation consecutive to the Ar transformation, and attribute this to the incomplete solution of the carbide at the critical temperature. This secondary effect, they say, was only obtained in steel in which the cementite had been coalesced. An explanation for this phenomenon was given in 1920 by English workers.[10] Whilst all research work is liable to criticism, one likes to see this criticism made, rather than that the work should be ignored.

In a further paper Chevenard and Portevin[11] regard the contraction immediately following the dilatation of transformation as being purely thermal, and cast doubt upon Honda's "two martensites" theory.

In an experimental investigation of the mechanical properties of steels at high temperatures,[12] E. L. Dupuy has spoilt an excellent paper by one important omission. After commenting upon the fact that certain experimental work of another was lacking in value owing to the small number of determinations, Dupuy himself fails to give the number of tests made in his own investigation. Apart from this really important fact, the paper and results are remarkably interesting. His curves, showing the variation of maximum stress and contraction with temperature, may be roughly divided into two categories: (1) Those in which the carbon is below 0·6%, and (2) those in which the carbon is greater than 0·6%. Steels of Class 1 show a maximum in the region of 300° C., both in the reduction of area and maximum strength. The most remarkable feature is, however, the sudden drop in the reduction of area between 750° and 1000° C. In the rolled and treated bars containing carbon 0·15%, this drop amounts to 50% of its value at 750° C. This, as Dupuy points out but does not attempt to impress, is an indication of beta iron. Indeed, from these results alone no one can seriously ignore the possibility of a beta state. It is not necessarily to be inferred that beta iron represents an allotropic modification, nor is it sufficient to regard it as a purely magnetic phenomenon, unless we associate with that magnetic change some distinct atomic or molecular change, which, whilst taking place, seriously weakens the metal. In Class 2 some extremely interesting results have been obtained. There is an almost continuous increase in the reduction of area between 500° and 1200° C., excepting for a small break in the curve at about 750° C.,

[9] *Comptes rend.*, 1921, **172**, 1490; *J.*, 1921, 514A.

[10] *J. Iron and Steel Inst.*, 1920, **100**, 527.

[11] *Rev. Met.*, 1921, **18**, 428; *J.*, 1921, 699A.

[12] *J. Iron and Steel Inst.*, 1921, **104**, 91; *J.*, 1921, 698A.

and another at 900° C. These curves for the higher carbon contents clearly show that the solution of the carbide and alpha to gamma change have but little effect upon the mechanical properties; that is to say, that no abrupt break in these properties is experienced.

Whilst commenting upon this question of beta iron, reference should be made to a short paper by K. Honda,[13] in which the author shows that the temperature of the Ar2 change is unaffected by the strength of the magnetising field.

Confirmation of Dupuy's work is afforded by the work of MacPherran,[14] who found that with a 3·5% nickel steel, the maximum tensile strength is developed at 315°–345° C. The presence of nickel, he found, lowered the temperature of maximum strength and lessened the ductility at higher temperatures. His results indicate that carbide-forming elements, such as chromium, tend to strengthen the steels at high temperatures. The high tensile strength of such steels as rustless confirms this view.

Roentgen Spectrographic Investigation of Iron and Steel and the Space Lattice Theory.

One of the most important discoveries of late years is undoubtedly that pertaining to the arrangement of atoms in space, and the application of the principles of Bragg to metallic structures.

The controversy raging over beta iron received its sudden solution in the hands of A. Westgren,[15] who showed, by means of the X-ray spectrographs of iron at different temperatures, that the so-called beta modification was crystallographically similar to alpha iron and of a cube-centred configuration. Gamma iron, examined both at a high temperature and in an austenitic structure in the cold, indicated a face-centred structure. The constitution of martensite was also dealt with, and it was clearly shown that in this constituent the iron existed in the alpha condition. No direct evidence was, however, obtained of the structure of the carbide of iron in any of the sections examined, but its constitution was pronounced as being complex.

In his lecture before the Sheffield Society of Engineers and Metallurgists, the writer put forward a suggestion relating to the arrangement of the carbon atoms in a quenched steel, which was as follows. The hardest steel known may be obtained by quenching from above the critical point a plain carbon steel containing 0·66% of carbon. A steel of this composition contains the equivalent of three atoms % of carbon, or 3 mols. of carbide of iron in 88 of iron. Taking it that in an unlimited number of cubes of iron 4 atoms are associated with each crystal of the face-centred

[13] *Ibid.*, 1921, **104**, 185; *J.*, 1921, 737A.

[14] Amer. Soc. Testing Materials, June 24, 1921.

[15] *J. Iron and Steel Inst.*, 1921, **103**, 303; *J.*, 1921, 392A.

type, it would mean that for every 3 mols. of carbide of iron there would be 22 cubes of iron, a ratio of 1 to 7·33, or approximately 1 to 8. The only way in which such a structure could be built up would be by assuming that at the point of contact of the corners of 8 cubes there was 1 mol. of carbide, which by forcing the iron atoms apart, in this manner brought about maximum distortion. It seems necessary to assume that the carbide would crystallise according to the form of carbon, that is as a tetrahedron ; and that if there were to be a homogeneous distribution of the carbide, there could not be as many as 4 atoms in contact, or in other words that up to a certain concentration the carbide must exist as free molecules. When the composition of the eutectoid—*i.e.*, 0·89% of carbon—is reached, the necessary 4 atoms are present, so that from that composition upwards it should be possible for the carbide to exist in the crystalline form.

It is known that with carbon higher than 0·89% it is possible by quenching from a high temperature to obtain some austenite. Austenite is regarded by the writer as gamma iron, in which the structure has been stabilised by the tetrahedronal space lattice of the carbide molecules. The saturation value of iron for carbide at 1130° C. is equal to 8 atoms % of carbon, which, assuming them to exist as carbide of iron, gives 8 atoms of carbon, or 2 tetrahedrons for every 68 atoms or 17 cubes of iron. Crystallographically the greatest number of tetrahedra that can be built into a cube is 2. Since it is, however, difficult to know of the exact arrangement of the tetrahedron in the cube, if we assume that relative to each tetrahedron there is but 1 atom of carbon, this then gives us for every 17 cubes 8 atoms of carbon, which is roughly as two is to one. The figure 17 is of some significance, since Westgren believes that with each carbon atom there are associated 17 iron atoms. By assuming that the crystallisation of the carbide within the iron structure stabilises that structure, an explanation of the greater ease with which the gamma state is preserved becomes evident.

Now with regard to the property of hardness, the molecular carbide, by forcing apart the iron crystals, thus causing distortion, will effect not only a hardness but likewise a decrease in specific gravity of the quenched steel, by giving an alpha iron in which the atoms are still kept apart by the carbide molecules. On the other hand, with a higher carbon content, whereas upon passing the critical point the carbon will in all probability temporarily be transformed into the molecular state, upon further heating the molecular carbide will force its way into the iron space lattice, thereby effecting a temporary expansion, due to the crystallisation of the molecular form, but when once crystallisation has completely taken place the iron will expand similarly to normal gamma iron.

The fact also that after the carbon has passed the value of 0·89% when first the crystalline modification becomes possible, precipitation of free cementite above the eutectoid temperature occurs is significant.

The tendency to assume that in all solid solutions the foreign metals (that is those in small amounts) must necessarily exist in a definite crystalline state is difficult to understand. One has only to think of a hypothetical case in which we have but one atom of one metal in, say, a ton of another. In this case no equilibrium could be possible, for one point cannot be homogeneously distributed over a volume. Working upon this analogy, then, it must be admitted that the first atoms of an element or molecules of a compound must exist in the free molecular or atomic state, rather than the crystalline. So that whilst in the case just considered it is not to be inferred that with each cubic space lattice of iron 4 carbon atoms must be assumed, there must be at least an equivalent of 4, in order that crystallisation can take effect.

The relatively enormous lowering of the electrical resistance of a metal brought about by the addition of small amounts of a second metal, is, moreover, explained on this basis. Assuming the added metal to be in an atomic condition, probably occurring as an adsorbed layer around the crystalline boundary, it is easy to see that the foreign metal, behaving similarly to a gas, would effect a relatively large lowering of the electrical resistance, and that when sufficient was added to form a crystalline unit, whilst part of the metal would still exist in this atomic state, further additions would go to form either a space lattice of its own, or in combination with the mother metal, thus bringing the lowering of the property discussed to an end.

Failure of Metals under Internal and Prolonged Stress.

A general discussion was held on the above question at the last meeting of the Faraday Society.[16] Many of the papers were of a general character, and certain of them of a more special nature. The result of this discussion is very difficult to sum up; many highly interesting facts and problems were brought to light, but one rather regretted that no complete decision was arrived at in any one connexion.

The first day consisted of a duel between the adherents of the amorphous phase and those who do not credit this hypothesis with the explanation of everything. W. Rosenhain, in his introductory address,[17] put forward in a very able and lucid manner his interpretation of the part played by the amorphous metal. This was

[16] *Trans. Faraday Soc.*, 1921, **17**, [1], 1 *seq.*
[17] *Ibid.*, 2.

followed by an exceedingly critical and able paper by W. H. Hatfield, who very rightly suggested that to agree with Rosenhain one must conclude that there are two distinct types of amorphous material, viz., one form produced by cold work—a hard form—and, secondly, a viscous form existing at the crystal boundaries in the original cast metal, the latter being capable of viscous flow. Obviously, as Hatfield suggested, one cannot have it both ways; it must not be assumed that under certain conditions this amorphous material is capable of flowing, and in another case that it acts as a hard cement, incapable of flow.

In a written contribution to the discussion, A. McCance[18] rightly pointed out that in the papers contributed no attempt had been made to analyse the mechanism by which internal stresses are produced in metals. McCance pointed out that a test-piece stressed beyond its elastic limit in tension had its elastic limit in tension raised, and its elastic limit in compression lowered by a corresponding amount, the position of equilibrium being shifted along the direction of compressive stress. Dealing with the matter from the standpoint of quenched steels, he says: "There is always present the stress resulting from the alteration in volume at the gamma to alpha inversion, but in addition there is the stress introduced by the quenching operation itself, which will produce stresses in any material which possesses a temperature coefficient of expansion. . . . On plunging a long heated rod in water, the outer portion commences to cool down and contract before the inner portion, and in doing so it produces a tensile stress circumferential to itself, and a compressive stress in the core. In a direction at right-angles to this, along the axis, these stresses produce corresponding tension and compression stresses respectively. If they reach such a value that they exceed the elastic limit at any time, deformation takes place, and reversed internal stresses are left in the material. In the longitudinal direction, in the outer portion, internal compression stresses will exist, and these will be balanced by internal tension stresses at the centre, since the stress integral across any section must be zero." It is clearly evident from this last contribution that there is no necessity of assuming any such state as the amorphous; to account for failure in stressed materials, it is indeed sufficient to consider the matter from the standpoint of opposing stresses. As long as these are balanced, failure will not result; but immediately this balance is disturbed, then failure is most likely to occur.

With reference to the intense hardness always assumed for the amorphous material, McCance pointed out that amorphous silica is softer than the crystalline variety, and it was used for galvanometer suspensions on account of the absence of viscous flow.

[18] *Ibid.*, 71.

The greater part of the papers read at this meeting were concerned more or less with special cases of failure; for instance D. Hanson[19] dealt with intercrystalline failure in boiler plates—failures which, as pointed out by him, seemed generally to result owing to the segregation of thin cementite films around the crystal boundaries. As to whether one must assume greater strength along the crystal boundary, or whether this results merely from crystal interlocking, has not been conclusively proved. At his Sheffield lecture the writer offered the suggestion that at the grain boundaries there existed a stronger attraction between the atoms due to the unsatisfied valencies of two layers of surface atoms, this suggestion being based on the Langmuir theory of adsorption. It might even be due to the forces of co-valency. This suggestion at least explains the action of corrosive reagents in preferentially attacking the grain boundary material, for it naturally assumes a greater surface of attraction, and therefore greater field of chemical activity.

Quite an excellent summary relating to the forces producing rupture in steel was given by J. N. Greenwood.[20] Owing probably to there being but little new material, and partly owing to the rather incomprehensive manner in which the case was stated, this paper did not come in for much discussion. As a general survey of the forces tending to cause rupture in steel, the paper is excellent and certainly merited greater attention than it received. With the exception of a certain few of the contributions, notably those by Hatfield, McCance, and Greenwood, one felt that but little had accrued from this discussion. Much food for thought was, however, provided, and if only certain of the contributors would make an impartial digest of the matter brought up, their views upon the causes and effects of internal stresses should be greatly modified.

Corrosion of Iron.

The corrosion of metals is a subject about which we know less and publish more than about any other.

A theory of corrosion seems to be part of the individual; every man appears to have his own view as to why corrosion takes place, and equally to ignore the views of others. It is interesting then to compare a few statements with regard to the effect of copper in steel, upon its corrosive value. F. K. Bell and W. A. Patrick[21] conclude from their experiments that copper has a marked retarding effect on the rate of solution in 27% solution of hydrochloric acid, as compared with pure reduced iron. A 50% solution of sulphuric acid gave erratic results.

[19] *Ibid.*, 91; *J.*, 1921, 104A.

[20] *Ibid.*, 123; *J.*, 1921, 105A.

[21] *J. Amer. Chem. Soc.*, 1921, **43**, 452; *J.*, 1921, 304A.

O. Bauer[22] also finds that copper lessens the corrosion of iron in atmospheric air, and also in sulphuric acid fumes, and O. W. Storey[23] suggests that steel ranges built of iron containing copper corrode less. E. A. and L. T. Richardson[24] state that copper increases the rust-resisting power of steel.

Contrary views are expressed by A. S. Cushman and G. W. Coggeshall,[25] who state that copper-bearing iron is less resistant to corrosion than copper-free metal, whilst J. A. Aupperle and D. M. Strickland[26] give values for the corrosion of steels in a solution containing 0·7% of sulphuric acid, 1·98% of ferrous sulphate, and 0·15% of ferric sulphate, the solution being continuously circulated and aerated. The loss in weight in sixty days was as follows:—Pure open-hearth iron, 0·622 oz. per sq. ft.; copper open-hearth steel (0·257% Cu), 0·75 oz. per sq. ft.; open hearth steel, 0·779 oz. per sq. ft.; Bessemer steel (0·224% Cu), 2·060 oz. per sq. ft.; copper acid open-hearth steel (0·209% Cu), 3·263 oz. per sq. ft.

One's pity goes out to the technical and commercial man who relies upon the scientist to assist him in this matter of corrosion. Experiments and determinations are legion, but the conclusions are worthless. Each investigator appears to employ the methods that appeal to himself, each takes for his purpose different types of steel, manufactured by different processes. Not content with this, it is usual for each individual to employ some special form of corroding reagent. What is the result of this? The publications and scientific press are flooded with innumerable results, all unstandardised and unco-ordinated, and therefore for practical purposes useless. Dealing with the question of the corrosion of iron as a whole J. A. N. Friend[27] formulates a colloidal theory of corrosion. The main features of his theory are as follows:—(1) The rate of corrosion is dependent upon sol formation. (2) The dissolved iron is originally present in the ionised ferrous state, but is rapidly converted into the sol of ferrous hydroxide, and afterwards oxidised to the higher hydroxide, this latter acting catalytically by oxidising metallic iron, itself undergoing reduction, and is subsequently re-oxidised by the oxygen of the air. He supports this theory by mentioning that substances such as strong electrolytes, which destroy and cause precipitation of the colloid, retard corrosion, whilst other substances, which assist in stabilising or forming colloids, increase the corrosive action.

If we accept this theory we must needs alter our definition of a

[22] *Stahl u. Eisen*, 1921, **41**, 37, 76; *J.*, 1921, 393A.
[23] *Trans. Amer. Electrochem. Soc.*, 1921, 13; *J.*, 1921, 220A.
[24] *Ibid.*, 55; *J.*, 1921, 262A.
[25] *Ibid.*, 249; *J.*, 1921, 350A.
[26] *Ibid.*, 167; *J.*, 1921, 350A.
[27] *Chem. Soc. Trans.*, 1921, **119**, 932; *J.*, 1921, 545A.

catalyst. One always assumed that a catalyst was a body which underwent no change during the reaction, but here we have a substance termed catalyst which undergoes alternate oxidation and reduction.

Another interesting point is with regard to the initial solution, previous to the formation of the colloid. If solution without any colloid is possible why bring into the theory a colloidal explanation?

Slags.

Research work upon slags, whether of blast-furnace or of steel-furnace origin, has been extremely limited during the year 1921. L. Blum[28] has quite reasonably pointed out that the basicity of a basic slag is limited to excess lime beyond that required to form tetracalcium phosphate and calcium monosilicate. He concludes that 4% of excess lime is sufficient for the purposes of desulphurisation and dephosphorisation.

J. E. Fletcher[29] emphasises the importance of graphical methods in consideration of slag compositions, and illustrates his results in this manner on every possible occasion. The author assumes that blast furnace slags are constituted of orthosilicates, which act as solvents with respect to the other constituents, dissolving free silica and alumina. In view of the work of Feild and Royster,[30] who have shown by means of viscosity determinations that in the liquid states the slag retains the constitution of the solid, this view is difficult to accept.

Fletcher makes the statement that there is always a tendency for the slag to become neutral, chemically speaking. This is as interesting as it is natural, the neutral state being of an eutectic composition, in which there will separate, upon cooling, the pure compounds in a free state. An eutectic composition is synchronous with the maximum entropy function, the change in Q at a constant temperature, T, being greatest during the solidification of an eutectic composition, and it is known that all bodies tend towards maximum entropy. There is then some scientific foundation for this statement.

Many of the suggestions put forward in this paper are somewhat of an empirical nature, and require further thought and investigation. The discussion on the paper is particularly interesting.

Processes and Treatment of Steel.

H. Brearley,[31] in a paper on the welding of steel, shows that a weld can rarely, if ever, be perfect. As a method of testing welded material he suggests the employment of an Izod impact test. He

[28] *Stahl u. Eisen*, 1921, **41**, 69; *J.*, 1921, 392A.

[29] *J. Iron and Steel Inst.*, 1921, **103**, 105; *J.*, 1921, 394A.

[30] U.S. Bur. Mines, Tech. Papers 187 and 189; *cf. J.*, 1918, 246A, 548A.

[31] *J. Iron and Steel Inst.*, 1921, **103**, 27; *J.*, 1921, 190B.

cites experiments made by himself, in which he drilled a hole in a steel ingot, filled up this hole with a close-fitting bar of the same material, and then rolled the composite mass together. From the value of the impact figures he shows that for a welded section the impact value would be less if the weld were perfect than if otherwise, an imperfect weld acting as a composite material. Owing to the welded portion tearing away at the weld immediately upon fracturing, the metal forming the second part of the weld will, so to speak, act as a backing, and add greatly to the apparent value of the Izod figure. Were the weld perfect it would break as one homogeneous piece, with a lower impact value. From results obtained after different treatments, the author calculates the comparative welding figures of four typical steels, *viz.*, low-carbon steel, nickel steel, nickel steel with low chromium, and a nickel-chrome steel, the mild steel giving the highest and the nickel-chrome steel the lowest figure. The author refers to sulphur in steel, and indicates that its value as a means of producing a sulphur print, and thereby giving an indication as to the manner in which the metal has been cast and worked, is perhaps greater than the detrimental properties conveyed upon the steel by this element.

Dealing with the dimensional effects of heat treatment of carbon steels, W. P. Wood[32] concludes from his experiments that, after a normal oil-hardening from 900° C., followed by tempering at 600° C., compared with the ordinary annealed steels, a hypo-eutectoid steel is shorter, an eutectoid steel the same, and a hyper-eutectoid steel longer after this treatment. His results agree with those of Andrew, Rippon, Wragg, and Miller.[33]

An interesting paper on case-hardening is contributed by H. Fay,[34] who supports the view that case-hardening is a nitrogenising as well as a carbonising process. Quoting from the work of other observers the author refers to a case in which Hurum found that after heating a low-carbon steel in a cyanide bath for 10 minutes at 830° C., the nitrogen content on the outside layer was 0·57%. By using Shimer's cyanide process it is stated that both carbon and nitrogen diffuse through iron at a temperature of 650° C., which is below the change point (the temperature of 650° C. is, however, so near to that of the transformation point, that this statement must not be accepted without question).

The nitrogen content is said to decrease with rise of temperature, the maximum content (0·579%) being arrived at at 750° C. As nitrogen is known to have an appreciable hardening effect upon iron it is quite possible that in using cyanide mixtures for case-hardening the reaction suggested does take place, for experimental

[32] *Chem. and Met. Eng.*, 1921, **24**, 345; *J.*, 1921, 261A.

[33] *J. Iron and Steel Inst.*, 1920, **101**, 493; *Ann. Repts.*, 1920, **5**, 244.

[34] *Chem. and Met. Eng.*, 1921, **24**, 289; *J.*, 1921. 220A.

results all point to solid carbon being unable to cement iron. Knowing that nitrogen will combine with iron to form a nitride, and that the only difficulty of forming this nitride lies in causing the nitrogen to diffuse into the iron; when we have a gaseous radicle CN, both reactions become possible.

The question as to whether oxygen is soluble in steel came under discussion, due to papers by J. E. Stead and J. H. Whiteley.[35] Proof was furnished both in the papers and in the discussion that oxygen, probably as oxide of iron, has a limited solubility in steel. Evidence of this was furnished by application of the cupric reagent, which showed unattacked areas where oxygen was suspected, and gave negative results when the same sample was reduced in hydrogen.

A. McCance in the discussion referred to some experiments of his own, in which the amount of oxide included in the steel was a function of the slag composition and the temperature of melting. It is a well-known fact that if time is allowed, an equilibrium exists between the oxide in the slag and the oxide in the metal, the distribution obeying the Nernst distribution law, so that by controlling the composition of the overlying slag it is possible to produce a steel comparatively free from this harmful constituent.

The existence of oxygen-bearing iron is also inferred by A. Matsubara,[36] who determined the equilibrium relations between CO, CO_2, and Fe at three different temperatures, and likewise studied the systems CO—CO_2—FeO, and CO—CO_2—Fe_3O_4. The system Fe—FeO—CO—CO_2—C has also been determined by V. Falcke.[37]

S. N. Brayshaw[38] describes at great length his method for the prevention of hardening cracks in a steel containing 1·1% of carbon, 0·8% of tungsten, and 0·2% of chromium. One gathers from this lengthy paper that the question of cracking largely depends upon the initial treatment of the tool. The figures given are so numerous and the descriptions so lengthy that unless one has a particular interest in this uncommon class of steel interest is apt to fade away before the end is reached. If, on the other hand, one does complete the perusal of this paper, the feeling that one has really done something hangs foremost in the mind.

New Steels.

Uranium steels are dealt with by H. S. Foote.[39] But little effect upon the transformation points is produced by addition of this

[35] *J. Iron and Steel Inst.*, 1921, **103**, 271-302; *J.*, 1921, 392A.

[36] *Trans. Amer. Inst. Min. Met. Eng.*, Oct., 1921; *J.*, 1921, 304A.

[37] *Z. Elektrochem.*, 1921, **27**, 268; *J.*, 1921, 545A.

[38] *J. Iron and Steel Inst.*, 1921, **103**, 131; *J.*, 1921, 393A.

[39] *Chem. and Met. Eng.*, 1921, **23**, 789; *J.*, 1921, 850A.

element up to 2·0%; further additions lower the changes and induce a martensitic structure. Uranium appears to induce the formation of sorbitic pearlite similarly to chromium. Speaking generally, it tends to emphasise the special properties induced by other special elements when added along with them.

A New Etching Reagent.

A new etching process is described by A. Fry.[40] The process consists in annealing the test piece for about half an hour at 200° C., and etching with a strong solution of cupric chloride in hydrochloric acid. For micro-sections the reagent consists of 40 c.c. of concentrated hydrochloric acid, 30 c.c. of water, 25 c.c. of ethyl alcohol, and 5 g. of crystalline cupric chloride. This reagent is said to show up strain effects remarkably well.

Mechanical Properties.

Two excellent papers by W. H. Hatfield[41] deal with the mechanical tests of numerous steels. The purposes of both these papers are alike In the first-mentioned the author attempts to impress the marine engineer with the well-established fact that better mechanical properties may be derived from certain alloy steels than can possibly be obtained from ordinary carbon steels. Many of the results given had been published previously, and were referred to in last year's report. Hatfield's results are reliable and his conclusions sound, and, as previously said,[42] he has the courage of his convictions, not being content with merely giving the actual properties of steels of varied compositions, but even going further, assigning to each particular steel its special use and method of employment. The steels considered cover a wide range of carbon, nickel, nickel-chrome, chrome, and chrome-vanadium steels. In the second paper special steels are dealt with from the standpoint of the Wöhler fatigue range. The method of conducting the Wöhler test is described and the fatigue values given. The author takes for his purpose a good selection of steels as used in the automobile industry, and in his conclusions makes the following comments: "For 10,000,000 revolutions, the safe range of stress for carbon steels used in the motor-car industry is from 12 to 18 tons per sq. in. For alloy steels the comparative figures are 21·5 to 28 tons. Here is indeed a sound argument for the extended use of high-tensile alloy steels for highly stressed parts." The figure of ten million, it should be remarked, is the number of reversals that a steel must stand without rupture, under a particular load. In other words,

[40] *Stahl u. Eisen*, 1921, **41**, 1090; *J.*, 1921, 660A.

[41] *J. West Scotland Iron and Steel Inst.*, 1921, **28** [5]; *J. Inst. Automobile Eng.*, 1921, 465.

[42] *Ann. Repts.*, 1920, **5**, 241.

the load under which the steel will just stand this number of reversals is the figure taken.

L. Aitchison[43] gives an exceedingly good account of the properties of chromium steels. He suggests replacing many special steels of other types by means of pure chrome-carbon steels. His tests show the great latitude possible by slight variation of the chromium and carbon content. He also describes the properties of chromium iron containing 11·7% of chromium, this being of a rustless nature. This alloy, after a treatment consisting of oil-hardening at 930° C., followed by a tempering at 750°, gives tensile results as follows: Yield point 27·0, maximum stress 36·7 (tons per sq. in.), elongation 31·0%, reduction of area 68·8%, Izod impact 87 ft.-lb.—a truly remarkable test for a practically carbonless material. Highly interesting are a series of test values given showing the comparative relation between chrome-vanadium steels and pure chrome steels, to which has been added an amount of chromium corresponding to the vanadium. These tests indicate that chrome-vanadium steels may be reasonably replaced by pure chrome-carbon steels containing an excess of chromium corresponding to the vanadium in the quaternary steels. During the discussion the remark was made that the engineer, after being told by one metallurgist of the great value of nickel-chrome steels, was now being told that pure chrome-carbon steels were as good if not better. What, then, was the engineer to do?

Conclusions.

Apart from the deplorable condition of the industry, the year 1921 has been somewhat deficient in original investigations. No revolutionary discovery has marked this period, nothing outstanding has been revealed; in fact, we have just passed through a very ordinary year. Papers in numbers have been read and have been discussed, but can we say that as a result of all this we are any nearer to the final goal, the age when a scientific explanation for all facts becomes possible?

Let us take as an example the discussion on internal stresses held under the auspices of the Faraday Society. Undoubtedly much that was new and valuable came to light; but if one were to attempt to summarise the result of this discussion, to come to any conclusions with regard to the real cause of internal stresses and the nature of such stresses, they would be utterly at a loss to know which school to follow. It is well-nigh impossible to reach a state of finality in anything; every hypothesis proposed and accepted must indeed be but a transient stage in our evolution, but when there exist two definite and different schools of thought, the matter becomes even more difficult.

[43] Inst. Automobile Eng., Nov. 10, 1921.

Then with regard to the adoption by engineers of special steels—that is to say high-tension steels—to replace the present class of ordinary mild steels. Hatfield in particular has been preaching their more extended use from the housetops; he has given large numbers of tests illustrating their superiority, and yet we are just where we were. This attitude of indifference on the part of engineers has done and is doing greater damage to metallurgical research than is generally realised. The metallurgist investigates, carries out innumerable tests, and concentrates the whole of his brain power upon problems connected with engineering materials, all to be paid for by this lethargic indifference. One would have thought that, industry having been slack, managers would have at once have turned their attention to research, in order when trade revives to be in a position to put on the market fresh steels with special properties, to be able to start up again with the help of new tools in the way of knowledge. This is not so, however; we progress when we are forced to progress, we adopt new methods when our competitors have installed them and captured our trade. Unfortunately most of these competitors are foreigners. The metallurgist is then in the unenviable position of an onlooker, who, seeing what is required, and at the same time having the knowledge and ability to act, is unable to do so because he has not the power. Is this always to be ?

THE METALLURGY OF THE NON-FERROUS METALS.

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There is little to record in the technical development of non-ferrous metallurgy during the past year. The depression which has so profoundly affected the whole of industry has prevented expansion of manufactures and the trial of new processes. Many important plants have been standing idle, whilst developments which have been projected have had to await a more favourable time. On the other hand, the scientific study of non-ferrous metals and alloys has been progressing rapidly, and this is a most hopeful sign, promising improvements in the extraction, treatment, and utilisation of metals as soon as circumstances permit, with consequent great advantages to the industry. In our own country the Non-Ferrous Metals Research Association is gaining in strength, and has already undertaken a programme of research which should result in great benefits to its members. This Association has adopted the wise policy of concentrating its energies on problems of fundamental importance rather than on minor shop difficulties, the solution of which is not the work of a co-operative body, although its central bureau is usually in a position to supply existing information from its stores of filed and classified papers. For the sake of the British metallurgical industries generally, it is to be hoped that this important research organisation will receive the fullest support from all firms connected with the manufacture and treatment of the non-ferrous metals. It is only by a large membership that such associations can obtain the resources necessary for an extensive campaign of investigation and for the maintenance of an efficient machinery for collecting and distributing technical information to its members.

The publications of the year include statistical pamphlets in the series issued by the Imperial Mineral Resources Bureau, dealing with aluminium, antimony, barium, cobalt, manganese, tungsten, and zinc, whilst the Imperial Institute has published monographs on the ores of silver, chromium, and lead. Attention should, perhaps, be called to an important monograph on the economics of the copper industry by F. W. Franke.[1] This is an exhaustive

[1] Munich, Duncker and Humblot, 1920.

work, and although European countries have only received a small part of the author's attention, the survey is most illuminating, and it is to be hoped that other metallurgical industries will in time be treated in a similar manner.

Gold mining has had to contend with serious difficulties, and in South Africa the world's economic condition has combined with labour troubles to hamper the progress of even the most productive mines, whilst the low-grade mines have found it difficult to continue working. One consequence has been that greater interest has been taken in the ores of base metals and in non-metallic minerals, in which the country is also rich.[2] Copper and tin mining are assuming importance in the Protectorate of South-West Africa.[3] An interesting change in the method of treating gold ores has been adopted by the Springs Mines Co. in the Transvaal.[4] In the new plant the stamp mill and amalgamation plant have been discarded, and the ore passes directly to the tube mill for treatment. A tube mill can deal with ore in the condition in which it comes from a gyratory crusher, and can grind it to such a fineness that cyanide extraction is rapid and complete. The results of such a simplification of the ordinary process will be interesting when compared with the standard method of working. Apart from this development there is little to record in the treatment of gold ores. R. Paulin[5] states that ball mills are inefficient in separating gold from quartz, and that roller mills or tumbler mills have advantages over them. Some experiments on cyanide solutions have been made by H. A. White,[6] who finds that wattle bark extract, in the presence of a minute quantity of alkali, is the cheapest and most efficient for the removal of oxygen, and by J. H. Johnson,[7] who finds that in highly alkaline solutions deposits of calcium carbonate and hydrated silica are liable to cause clogging of the zinc precipitation boxes.

The scarcity of platinum is a serious matter for many chemical industries. Russia and Colombia produce about equal quantities of the metal, and the production of all remaining countries is insignificant in proportion.[8] A few new discoveries have been made in Canada, and the presence of very small amounts in some of the rocks of Cornwall has been reported, but the quantity is insufficient to pay for working. The Russian production is not very far short of its level before the war.[9] As there is no sign of any new source of importance, it becomes an urgent question whether the use of

[2] *J.*, 1921, 32R.
[3] *J.*, 1921, 150R.
[4] *J.*, 1921, 389R.
[5] *Chem.-Zeit.*, 1921, **45**, 285; *J.*, 1921, 304A.
[6] *J. Chem. Met. Soc. S. Africa*, 1920, **21**, 105; *J.*, 1921, 263A.
[7] *Ibid.*, 58; *J.*, 1921, 48A.
[8] *J.*, 1921, 434R.
[9] *J.*, 1921, 471R.

platinum in jewellery, for which other metals are at least equally suitable, should not be forbidden, in order to free this essential metal for its legitimate uses in industry.

Experiments on the mechanical concentration of Silesian lead and zinc ores are described by W. Gross and W. Goy.[10] The bar form of screen, as used in Schubert's patents—the bars being shaped like fire-bars—gave the best results. The Schuchardt sieve and plates with conically-bored perforations, the cones widening downwards, came next in order. The free opening and the pressure in the plates above the screen are the two principal factors in determining the efficiency of the plant.

The theory of the settling of particles in concentration processes is discussed mathematically by K. Kegel.[11] The velocity of fall in a confined space is equal to the velocity in an unconfined space in the same medium multiplied by the ratio of the smallest unoccupied cross-section to the total cross-section. It follows that specifically heavy small particles fall more rapidly in a settling tank than larger particles of lower specific gravity.

An account of experiences with the Gröndal method of flotation is given by A. Macco.[12] During and since the war four plants on this system were erected in Germany for the purpose of dealing with low-grade ores, and the results suggest that many poor ores may be economically treated in the same way. The ore is crushed in a wet tube mill to pass a 120–200 mesh sieve, a small quantity of a heavy oil (0·2–0·3 kg. per ton) being added drop by drop towards the end of the operation. The mixture is then passed to a large funnel-shaped vessel, in which the coarse particles settle whilst the overflow passes to the flotation apparatus proper, which consists of a series of wooden chambers of simple construction without moving parts. The froth is produced by blowing compressed air through the chambers. A minute quantity of a secret chemical is added as a flotation agent. The foam is broken up by a spray of water and the separation of the water is best effected by pouring into shaking vessels, each of which tips its contents into the next. About nine-tenths of the concentrate is thus reduced to a water content of 12%, half of which is removed by air drying, whilst the remaining one-tenth is filtered through coke. The water which separates is used over again. As an example of the results obtainable, the galena blende ore of the Friedrich-August-Hütte, containing 36·8% of barytes, yielded 85–90% of its zinc, 87–93% of its lead, and 90% of its silver in the form of a concentrate containing only 5% of barytes. At Gottesgabe an ore containing only 1·5% of copper yielded a concentrate with 32%. Experiments

[10] *Metall u. Erz*, 1921, **18**, 121, 152, 177.
[11] *Ibid.*, 1920, **17**, 535.
[12] *Ibid.*, 1921, **18**, 197.

were made with laboratory mixtures of copper pyrites and sand by W. S. Morley,[13] to determine the effect of various flotation agents. Viscous substances, such as coal tar, gave bad results. The addition of xylidine with some of the organic chemicals now in use was found to be favourable.

Some of the complex lead-zinc ores of Idaho, according to C. A. Wright, J. G. Parmelee, and J. T. Norton, are very difficult to concentrate, on account of the intimate admixture of the metalliferous minerals with the gangue.[14] Even when crushed to 200-mesh, the constituent minerals are imperfectly separated, but it appears that flotation gives a better separation than gravity concentration. Ores approximately similar in composition behave differently towards flotation agents, the best flotation of galena being obtained in alkaline solutions, so that by adding sodium carbonate or some equivalent salt, together with tar or charcoal, galena may be floated from blende or pyrites, and by subsequent addition of a copper salt and pine oil the blende may be floated. Chalcopyrite is separated from a schistose gangue by addition of coal tar and wood creosote. Antimonial silver ores were found to be difficult, and sodium sulphide and cyanide proved to be useful additions to the pulp before floating by means of vegetable or mineral oil.

An unusual method for the separation of silver from ores containing that metal and manganese is described by J. A. Carpenter.[15] Roasting with salt at 1000° C. converts silver, copper, lead, and gold into chlorides, which are volatilised and collected by means of a Cottrell electrostatic plant. The yield is stated to be 95–99%, with a small consumption of fuel, oil being used for the purpose.

Smelting Equilibria.

The methods of thermal analysis and microscopical examination, which have been so fruitfully employed in the study of alloys, have been less frequently utilised to throw light on the processes of smelting, although isolated workers have obtained good results. A series of systematic studies by W. Guertler and K. L. Meissner[16] is now in course of publication, dealing with the relations between various pairs of metals and sulphur. When the metals are copper and lead, cuprous sulphide is the first to be formed, followed by lead sulphide and lastly by cupric sulphide. Although copper and lead are immiscible in the liquid state, the presence of sulphides causes them to emulsify, so that in practice a single layer of metal is obtained in place of two. When the two metals are copper and bismuth, the upper layer consists of cuprous sulphide with only a

[13] *Trans. Amer. Inst. Min. Met. Eng.*, 1921 ; *J.*, 1921, 702A.
[14] *U.S. Bureau Mines, Bull.* 205 ; *J.*, 1921, 852A.
[15] *Eng. and Min. J.*, 1920, **110**, 898 ; *J.*, 1921, 48A.
[16] *Metall u. Erz* 1921, **18**, 145, 358, 410, 438 ; *J.*, 1921, 352A.

little bismuth, copper having a greater affinity for sulphur than bismuth. It is therefore impossible to remove bismuth from copper by melting with sulphide. Sulphur decomposes copper antimonide, forming cuprous sulphide and free antimony, whilst antimony sulphide reacts with metallic copper to form cuprous sulphide and copper antimonide, according to the proportions. Manganese has a greater affinity for sulphur than even copper, and this affinity is not modified by the presence of iron. Manganese and cuprous sulphides form a eutectic.

Some binary systems of sulphides have also been investigated in Japan. The sulphides of antimony and silver are found by K. Konno[17] to form a single compound, Sb_2S_3,Ag_2S, known in nature as miargyrite, without solid solutions. D. Iitsuka[18] shows that antimony and lead sulphides form no less than four compounds, all of which occur as minerals, whilst the sulphides of antimony and bismuth are found by Y. Takahashi[19] to form a continuous series of solid solutions.

Sintering being such an important process in modern ore treatment, some interest attaches to a study of the sintering process by K. Endell.[20] Not only low-grade fine ores but also flue dusts and other waste products have to be conglomerated for treatment in blast furnaces etc., and sintering often proves to be superior to briquetting. Chemical reactions take place between the solid materials, and true sintering, which involves the appearance of a small quantity of a liquid phase, is largely determined by these previous reactions. Both the taking of heating curves and direct observation by the heating microscope may be used to study the process. In the microscopical observations the beginning of sintering is marked by contraction of volume and rounding of the edges.

ZINC.

The electrolytic treatment of zinc ores continues to be a subject of discussion. The plant of the Anaconda Copper Mining Company is described by F. Laist and others.[21] Oxide roasting having proved unsatisfactory owing to the acid plant being unable to supply sufficient leaching acid, the furnaces were altered for sulphate roasting. Even with a very high iron content the proportion of zinc soluble in 2% sulphuric acid may be as high as 82% provided that the temperature does not exceed 600° C. McDougall furnaces give the best results, especially when provided with the Cottrell precipitating device, which returns not only dust but sulphur

[17] *Mem. Coll. Sci. Kyoto*, 1920, **4**, 51.
[18] *Ibid.*, 1920, **4**, 61.
[19] *Ibid.*, 1920, **4**, 47.
[20] *Metall u. Erz*, 1921, **18**, 163; *J.*, 1921, 394A.
[21] *Chem. and Met. Eng.*, 1921, **24**, 245; *J.*, 1921, 182A.

trioxide to the furnace. The leaching process is complicated, a series of tanks being used and two main stages being adopted, using first a neutral and then an acid solution. Zinc dust (made specially in an oil-fired atomising plant) is used for the final removal of copper, but a large part of the copper has been precipitated in the first stage by the bases. Rolled sheet aluminium cathodes and cast lead anodes are used in the electrolytic tanks, the latter only requiring cleaning every month or six weeks. The cathodes are easily stripped and only require washing and wire-brushing. The zinc is melted in coal-fired furnaces. This is now by far the largest electrolytic zinc plant in the world, the Australasian Zinc Co. coming second and the Trail plant third, there being no other works comparable with these.

The application of similar methods to low-grade zinc ores in Japan is described by M. Namba.[22] The consumption of the metal in Japan is too small to justify a large smelting industry, and wet methods are to be preferred. The sulphide ore is roasted and pulverised and extracted with a 20% solution of sodium bisulphate, heavy metals being removed from the filtered solution by means of zinc dust. After the usual oxidation and precipitation of iron and manganese, zinc hydroxide could be prepared from the filtrate by a process described by the author, using milk of lime as the precipitating agent, and taking advantage of physical changes in the state of agglomeration of the hydroxide and of calcium sulphate. Alternatively, the purified solution may be used for the electrolytic extraction of zinc.

There have been many papers on the distillation process for zinc. O. Mühlhaeuser, who has made frequent studies of the efficiency of the process, has used an experimental retort furnace to determine the main sources of loss,[23] and finds that the loss in the residues remains practically constant during the use of the retort for successive charges, but that the loss of vapour from the receiver is large at first and diminishes as the retort is used. The loss through cracks also diminishes in the same way. The author is of opinion that insufficient attention is paid in the industry at present to the sources of avoidable loss, and that much study will be necessary. The largest losses are due to the combination of zinc oxide with the clay of the retort, forming spinel minerals. This occurs when the retort is first used, and may then amount to 25% of the zinc in the charge, but the clay is soon saturated, and in the last charges this loss is not more than 1%.

The methods to be followed in the valuation of zinc ores, due regard being paid to the losses which occur in the smelting process when certain impurities are present, are discussed in an elaborate

[22] *J.*, 1921, 279T.

[23] *Metall u. Erz*, 1921, **18**, 145; *J.*, 1921, 305A.

series of articles by Paul.[24] A complex formula is obtained which involves not only the zinc content and its price, but also the sulphur content, the specific gravity of the ore, and the cost of unit volume of the furnace. This is considered to represent the true value much more nearly than the usual formulæ. A mechanical charger for zinc retorts, similar in principle to the overhead charger used in open-hearth steel works, is described by J. Thede.[25] This machine, introduced into Belgian works, allows each retort to distil a much larger quantity of zinc than when hand-charging is practised. A study of the formation of zinc dust has been conducted on a laboratory scale by O. Ravner,[26] who concludes that it is better, in order to avoid the formation of dust, to keep the temperature of the receiver a little above, rather than below, the melting point, and that the path of the vapour before condensation should be as short as possible. The presence of sulphur in the charge increases the amount of dust. Electric furnaces are found by the same author[27] to yield a dust containing more oxide and sulphide than that from retorts. A good recovery of zinc is obtained by melting the dust under a flux of zinc and sodium chlorides, or of zinc and calcium chlorides, the latter giving a recovery as high as 91·6%. H. Paweck[28] recommends the electrolytic recovery of zinc from dust by dissolving in dilute sulphuric acid and purifying in the usual way before electrolysis. This method is particularly suitable for the dust obtained when brass residues are smelted for the recovery of copper, which contains both oxide and copper.

The recovery of zinc from lead blast-furnace slags is described by G. Courtney.[29] Passing the slag through the blast-furnace with coke and limestone allows of the recovery of 60% of the zinc as fume, whilst approximately the same amount is recovered by heating in an electric resistance furnace without adding any reducing agent.

ALUMINIUM.

The metallurgy of aluminium has perhaps received more attention than that of any other metal during the past year, especially in France and Germany. The monograph by C. Grard, which has appeared in an English translation,[30] deals fully with the mechanical properties of the metal and its alloys, but gives only a meagre account of the manufacture and economic aspects. On the other

[24] *Metall u. Erz*, 1920, **17**, 439, 475, 514; 1921, **18**, 59, 126; *J.*, 1921, 305A.

[25] *Ibid.*, 1921, **18**, 262.

[26] *Chem. and Met. Eng.*, 1921, **24**, 932; *J.*, 1921, 514A.

[27] *Ibid.*, **24**, 922; *J.*, 1921, 514A.

[28] *Z. Elektrochem.*, 1921, **27**, 16; *J.*, 1921, 263A.

[29] *Proc. Austral. Inst. Min. Met.*, 1920, 75; *J.*, 1921, 473A.

[30] London, Constable, 1921.

hand, in view of the importance of aluminium to France, which possesses the principal deposits of bauxite, an exhibition was held in May last under the auspices of the Société d'Encouragement, devoted to the manufacture and applications of the metal, and two issues of the *Revue de Métallurgie* are mainly occupied by an account of the exhibits and by reports of the lectures given in illustration and explanation of them. The exhibition, described in detail by R. Guérin,[31] showed the historical development of the manufacture, the nature and distribution of the ore supplies, and the very numerous applications of the metal and its alloys, ranging from chemical and brewery plant to electrical machinery and aircraft. A good account of the methods of manufacture is given by L. Guillet.[32] The important operation of purifying the bauxite before electrolysis is nearly always performed by the Bayer process, using caustic soda, but the method of Peniakoff, consisting in the use of sodium sulphate, forming sodium aluminate and sulphur dioxide, the sodium being recovered as carbonate when the alumina is precipitated by carbon dioxide, was in use in two works which were destroyed by the Germans, at Selzaete (Belgium) and Menessis (Aisne), respectively. None of the methods depending on the formation of nitride has proved commercially successful.

British Guiana, which has extensive deposits of bauxite and also large sources of water power, may become an important centre of production. The United States and Norway have increased their producing capacity during the war. France is second only to the United States as a producer of aluminium, but Switzerland, Norway, and Canada approach it very closely.

A review of the prospects of the aluminium industry in Germany by R. Sterner-Rainer,[33] states that before the war Germany possessed only a single small factory in which the metal was produced, this being a branch of one of the Swiss works. Owing to the scarcity of the metal during the war, and the difficulty of obtaining it from Switzerland, no fewer than seven works were established, one of which, near Berlin, was producing aluminium at the rate of 3500 tons per annum by the end of 1915. As Germany has only scanty water power, the works, mostly in the neighbourhood of Cologne, were supplied with power generated from lignite, and conveyed through aluminium conductors. The total capacity for aluminium production in Germany now amounts to nearly 100,000 tons per annum, but the actual production is about 15,000 tons, one-third of which is exported. The main difficulties are the absence of native supplies of bauxite, the deposits in Istria and Dalmatia being small and costly, whilst the low-grade ores of

[31] *Rev. Mét.*, 1921, **18**, 539.

[32] *Ibid.*, 1921, **18**, 459.

[33] *Z. Metallk.*, 1921, **13**, 353; *J.*, 1921, 380R.

Hesse and from near Salzburg are difficult to work, and the fact that water power has not yet been employed, although it is thought that Southern Bavaria and German Austria could generate electric power at a reasonable cost. There is a great demand for aluminium in the country, especially for electrical purposes, but it remains to be seen whether the works, established to meet urgent war requirements, can continue to operate under competitive conditions.

No technical advances of any importance have been made in the processes of manufacture, but a new metal known as Aludur, having a Brinell hardness of 80 and stated to have excellent mechanical properties as well as increased resistance to corrosion, claims to be aluminium improved by mechanical and thermal treatment of a secret character. The use of aluminium alloys is on the increase, and it is hoped to replace copper, which has to be imported at great expense, in many of its applications by aluminium. Attempts are being made to devise a suitable method for the extraction of the metal from clay, but so far without success, although on a laboratory scale the operation has often been performed. The yields in practice appear to be small.

The Héroult process for the reduction of alumina to the metallic state has remained practically unchanged since its introduction, and there is no immediate sign of any important modification. Aluminium is peculiar in the fact that it cannot be refined after reduction without great difficulty, so that any necessary processes of purification must be applied to the ore. For scientific purposes, however, it is desirable to obtain metal of a high degree of purity, and experiments in this direction have been described by F. and W. Mylius.[34] Fractional crystallisation from the molten state yields an improved metal, provided that the quantity of iron and silicon (the most usual impurities) is small in the first place, the impurities remaining concentrated in the portions last to solidify. By stirring during crystallisation, and so obtaining a granulated metal, and then extracting with dilute hydrochloric acid, the iron may be almost completely removed, and the yield is much higher than by any method of fractional solidification. Using commercial aluminium with 99·58% Al, this method of extraction gives a yield of 50% of metal of 99·9% purity. The resistance of the metal to chemical attack is a direct function of its degree of freedom from impurities.

An interesting contribution to the metallurgy of aluminium is contained in two papers by R. J. Anderson and J. H. Capps from the United States Bureau of Mines, dealing with the gaseous atmospheres in various types of furnace used in the melting of aluminium.[35] Samples were drawn off from each furnace at regular

[34] *Z. anorg. Chem.*, 1920, **114**, 27 ; *J.*, 1921, 150A.

[35] *Chem. and Met. Eng.*, 1921, **25**, 54 ; *J.*, 1921, 587A.

intervals by means of a mercury apparatus. In the stationary open iron pot furnace, the metal is only in contact with air, and the extent of oxidation or nitride formation depends only on the temperature. In closed iron pot furnaces air and a little carbon dioxide are present, whilst in a gas-fired crucible furnace, the crucible having no cover, the atmosphere consists mainly of nitrogen with some hydrogen and oxides of carbon, varying with changes in the supply of air and gas. An oil-fired reverberatory furnace was found to have a distinctly oxidising atmosphere, whilst closed oil-fired cylindrical or egg-shaped furnaces contain more carbon dioxide. A Baily granular resistance electric furnace contained comparatively little carbon monoxide, owing to the low temperature, the same furnace when melting brass containing a much higher proportion. An indirect arc rocking electric furnace of the Detroit type gave entirely different results. The dross formed contained carbide as well as oxide and nitride, and cyanogen was evolved. The atmosphere contained as much as 20–40% of carbon monoxide, which may perhaps react with aluminium to form oxide and carbide, although such an atmosphere would be inactive towards copper or brass. The action of gases on aluminium at the temperatures employed in the foundry has been very little investigated.

The paper by Guillet, already quoted, contains a full bibliography of aluminium, together with a useful account of the chill moulds used in casting aluminium and its light alloys. In casting motor pistons, as metallic cores are impracticable, cores made of fine sand bound with either oil or sodium silicate are used.

The density of solid and liquid aluminium has been determined accurately by J. D Edwards and T. A. Moormann.[36] The density of pure annealed aluminium is very close to 2·70, falling regularly with increasing temperature until the value 2·55 is reached at the melting point. For determinations in the liquid state, a silica sinker, weighted by having an iron cylinder sealed into it, was at first employed, but was found to give inaccurate results owing to chemical action between the silica and metal, so that a different method was adopted. The vessel used was a double graphite crucible, the outer portion serving as a metallic bath to maintain a constant temperature, whilst the inner portion was of known capacity and was fitted with an accurately adjusted lid. This portion being filled with aluminium at a temperature slightly below that required, the metal expanded on heating, any excess escaping through a fine groove under the lid. The outer vessel was then emptied, and the crucible and its contents weighed. The expansion of graphite being known, the density could be calculated. A shrinkage of 6·6% takes place in the melting of aluminium, the

[36] *Ibid.*, 1921, **24**, 61; *J.*, 1921, 119A.

density of the liquid then being 2·382. At higher temperatures the density falls quite regularly, reaching 2·289 at 1000° C.

The piping of aluminium ingots has been studied by J. D. Edwards and H. T. Gammon,[37] a graphite crucible being completely filled with the molten metal and a hot iron plate then pressed down so that a known volume of liquid was enclosed. After cooling, the volume of the pipe was determined by filling with mercury. Whilst pure aluminium gives a pipe of 7·7%, an alloy with 8% of copper gives only 3·8%, although the shrinkage on solidification is the same in both cases. The reason for this is that the total contraction of the pure metal is represented by the volume of the pipe, whilst in the alloy part of the contraction is taken up by a readjustment of the shell formed at first, so that a considerably shorter ingot is obtained. The pipe diminishes with increasing copper content to about 10%. The eutectic, which contains 31% of copper, solidifies at a constant temperature and consequently shows much piping.

The use of aluminium in place of copper for electrical purposes in France is strongly urged in the national interest by E. Dusaugey.[38] Copper must be imported from abroad, whilst all the aluminium required can be produced at home from native ores. For long-distance transmission lines, one of the most important practical applications, the supports required need be only of the same height as for copper when the span does not exceed 50–80 metres, but when the span is 100–200 metres higher supports are necessary, on account of the greater sag. This difficulty may be overcome by providing the cable with a core of doubly galvanised steel wire. Specifications for such complex cables of two different types have been adopted in France, and the amount of sag is shown to be considerably less than with copper cables, and therefore much less than with aluminium cables without reinforcement. One such cable has been in use for the last three years, conveying current at 60,000 volts, and has shown no deterioration. It remains to be found by experiment whether such cables are capable of transmitting the high-frequency currents used in multiple telegraphy and telephony. The paper contains extensive tables showing the comparative physical and mechanical properties of copper and aluminium conductors. Records of the experience of a number of German electrical works with aluminium transmission lines have also been published by Wunder.[39] The mechanical properties of such lines appear to be quite satisfactory. Where difficulties have occurred the cause has usually been chemical deterioration, either at the points of support, where contact with other materials occurs,

[37] *Ibid.*, 1921, **24**, 338; *J.*, 1921.
[38] *Rev. Mét.*, 1921, **18**, 559.
[39] *Z. Metallk.*, 1921, **13**, 179; *J.*, 1921, 515A.

or at welds. Great care in making welds and junctions is required, and all joints and contacts should be well protected by a coating of a flexible insulating varnish.

Magnesium has been used to a limited extent in place of aluminium for engineering construction, this exceedingly light metal having excellent mechanical properties in the form of sheet, whilst it is easily protected in the mass against oxidation by a thin layer of varnish. Care has to be taken in the machine shops on account of the ready inflammability of magnesium turnings.[40]

Aluminium vessels are stated by Trillat[41] to be very suitable for use in the brewing and dairy industries, but the metal must be well rolled and polished, otherwise micro-organisms may lodge in the porous portions. It has been shown that there is no chemical attack by the acids of beer or milk, but washing with soda must be avoided and all vessels must be washed out after use, especially when salt has been used, as in cheese making. Aluminium condensing worms have been successfully used in distilleries and casks of the same metal may be employed, except for red wines, in which precipitation of the colouring-matter may take place.

The most important contribution to our knowledge of light aluminium alloys that has been made for some time is the eleventh report to the Alloys Research Committee by W. Rosenhain, S. L. Archbutt, and D. Hanson.[42] Many of these alloys are characterised by secular changes, known as age-hardening, which were first observed in duralumin. In this report the phenomenon has been definitely related to the solubility of magnesium silicide, Mg_2Si, in the solid alloys. The solutions obtained by quenching are unstable and gradually change to a very intimate mixture of aluminium and the silicide which remains without further alteration, certainly for a period of years. Ageing at about 200° C. gives better mechanical properties than are obtained at a higher or a lower temperature. The age-hardening of copper-aluminium alloys containing no magnesium is much less striking, although the compound $CuAl_2$, to which American observers have attributed the effect, does behave in a somewhat similar fashion. Alloys containing a larger percentage of zinc are much less susceptible to change. The increase of strength on ageing is not accompanied by any loss of ductility. Other papers on the age-hardening of aluminium alloys have been published recently, including one by C. Grard,[43] which contains many mechanical tests, but none are of equal importance to this report.

A remarkable alloy described in the report is that known as

[40] *Z. Metallk.*, 1921, **13**, 316.

[41] *Rev. Mét.*, 1921, **18**, 597.

[42] *Proc. Inst. Mech. Eng.*, August, 1921; *J.*, 1921, 851A.

[43] *Rev. Mét.*, 1920, **17**, 286; *J.*, 1921, 13A.

"Y," containing 4% of copper, 2% of nickel, and 1·5% of magnesium. Heat-treated castings of this alloy are specially resistant to stress, either direct or alternating, at high temperatures, and are therefore very suitable for engine pistons. A cheap and useful alloy of high tensile strength contains 3% of copper and 20% of zinc.

Several series of ternary aluminium alloys have been studied, so far as concerns their casting properties and mechanical strength, by M. Waehlert.[44] A useful account of the process of freezing of aluminium alloys containing copper is given by J. D. Edwards.[45] The densities of several alloys in the solid and liquid state have been determined, regular curves being obtained, and from these results the possible segregation during freezing has been calculated. Among minor investigations may be mentioned the study of the influence of cerium on aluminium and its light alloys by J. Schulte,[46] the results showing that comparatively little advantage is gained by the addition of that expensive metal, and one on the influence of iron on aluminium castings by L. Guillet and A. Portevin,[47] increased hardness and brittleness being observed. An alloy for which large claims are made is known as silumin.[48] It is stated to contain 14% of silicon without other alloying elements. It is suggested that it might be prepared by a direct process of electrolysis, and if this claim were to be substantiated it might be possible to utilise some of the deposits of bauxite which are at present rejected on account of their high silicon content. Some form of heat-treatment appears to be necessary.

Copper Alloys.

Several papers on matters connected with the brasses were read at the autumn meeting of the Institute of Metals. The relation of the density to the composition and to the casting conditions has been determined by T. G. Bamford,[49] who finds a considerable divergence between the values for alloys cast in sand and in chill moulds respectively over certain ranges of composition. R. Genders[50] recommends the use of a fireclay dozzle in casting brass ingots, and it is surprising that this simple device, so familiar in steel crucible melting, has not been more widely adopted in the non-ferrous industries as a means of obtaining sound ingots. The same author[51] has investigated the defect often found in extruded brass rods, and concludes that it is caused by mechanical stresses

[44] *Metall u. Erz*, 1921, **18**, 298; *J.*, 1921, 547A.
[45] *Chem. and Met. Eng.*, 1921, **24**, 217; *J.*, 1921, 182A.
[46] *Metall u. Erz*, 1921, **18**, 236; *J.*, 1921, 473A.
[47] *Rev. Mét.*, 1920, **17**, 753; *J.*, 1921, 83A.
[48] *Z. Ver. deut. Ing.*, 1921, Nov. 5.
[49] *J. Inst. Metals*, 1921, **26**, 155; *J.*, 1921, 700A.
[50] *Ibid.*, 1921, **26**, 139.
[51] *Ibid.*, 1921, **26**, 237; *J.*, 1921, 700A.

due to the mode of flow. He recommends the use of a hollow ram through which the extruded rod can issue, but this is open to the objection that buckling would take place very readily. It was shown in the discussion that where sound ingots were used and the parts of the press were properly proportioned, extrusion defects were rare. Some further light has been thrown on the transformation of brasses at 470° C. by determinations of the specific heat by F. Doerinckel and M. Werner.[52] The discontinuity presented by this property at 470° C. mostly disappears on annealing, and the specific heat then varies in a linear manner with the temperature. F. Doerinckel and J. Trockels[53] have determined the work done in deforming brass of various compositions at high temperatures. Hot-working is possible even with 28% of zinc, the work required at 800° C. being one-eighth of that at 200° C. The work increases with increasing zinc content up to 15% and then rapidly diminishes, becoming very small in the two-phase region of composition. The formulæ of Guillet, usually adopted for the calculation of the 'equivalent' quantities of other metals replacing zinc in complex brasses, are challenged by W. Guertler,[54] who seems to overlook the fact that the formulæ are only intended for use when the quantity of the added element is too small to give rise to the formation of a new constituent.

The effect of several impurities on the properties of gun-metal and similar alloys has been studied. R. T. Rolfe[55] concludes that the addition of lead up to at least 1% improves the properties of Admiralty gun-metal, especially in the form of sand castings, but that alloys consisting only of the alpha phase are somewhat weakened by lead, although their working quality is improved. The supposed improvement of the strength of gun-metal by the addition of lead is probably due to the deoxidising action of the added metal, and it is the general experience of founders that where adequate precautions are taken to avoid oxidation, much better mechanical tests are obtained without lead. J. Czochralski[56] finds that lead, even up to 6%, improves the fluidity and machining quality without adversely affecting the mechanical properties, but this author states that such quantities of lead pass into solid solution, and that free lead does not make its appearance under microscopical examination until the quantity approaches 10%, an observation quite inconsistent with previously accepted data. Czochralski has also examined the effect of increasing proportions of antimony,[57] and of arsenic[58] on

[52] *Z. anorg. Chem.*, 1921, **115**, 1; *J.*, 1921, 473A.
[53] *Z. Metallk.*, 1920, **12**, 340; 1921, **13**, 305; *J.*, 1921, 305A.
[54] *Ibid.*, 1921, **13**, 128.
[55] *J. Inst. Metals*, 1921, **26**, 85; *J.*, 1921, 700A.
[56] *Z. Metallk.*, 1921, **13**, 171; *J.*, 1921, 515A.
[57] *Ibid.*, 1921, **13**, 276; *J.*, 1921, 547A.
[58] *Ibid.*, 1921, **13**, 380; *J.*, 1921, 815A.

gun-metal, arriving at the conclusion that these impurities are innocuous below a limit of 0·3% of each.

Evidently with the object of discovering a thermo-element of sufficiently high efficiency to serve as a source of power, the German Coal Research Station has experimented with alloys which seemed to promise a more favourable thermo-electric power and ratio of thermal to electrical conductivity than those usually employed, and the phosphorus-copper alloys have been examined in this way by G. Pfleiderer,[59] with disappointing results. The highest values have, so far, been obtained from alloys of antimony and cadmium in atomic proportions, examined by F. Fischer and G. Pfleiderer.[60] These alloys change their properties in a high degree on heat treatment.

ZINC AND ITS ALLOYS.

The high cost of copper has led to many attempts to replace copper alloys, such as brass and bronze, by alloys containing some cheaper metal as their principal constituent. Among these, zinc has received most attention, aluminium having been dealt with above. The variation of properties of pure rolled zinc with the size of grain and mechanical condition has been studied by D. H. Ingall,[61] who shows the great increase in strength produced by cold-working, and the grain growth, associated with brittleness, produced by annealing at 200° C. Many experiments have also been made with this metal by E. H. Schultz and several collaborators.[62] The foliation sometimes observed in the sheet metal is attributed rather to differences in the method of rolling than to the presence of any particular impurity, and this is the experience of other workers, although the defect has not been fully explained. It appears that rapid reduction by heavy drafts is disadvantageous. The best working temperature is 120° C. The tensile strength is considerably improved by alloying with copper up to 2·5% or with aluminium up to 4·5%, but the ductility is diminished, copper being the better alloying metal of the two. For cast alloys, such as shell fuses, E. H. Schulz[63] finds that 4–6% of copper and 2–3·5% of aluminium may be added, whilst for some castings these quantities may be slightly increased. The alloys must not be overheated, and should be cast in chill moulds, with large heads. Lead, iron, and tin are all injurious impurities. A metallographic investigation of the alloys of zinc with limited amounts of copper and aluminium has been conducted by J. L. Haughton and K. E. Bingham.[64] The

[59] *Ges. Abh. Kennt. Kohle*, 1919, **4**, 409 ; *J.*, 1921, 223A.
[60] *Ibid.*, 1919, **4**, 440 ; *J.*, 1921, 223A.
[61] *J. Inst. Metals*, 1921, **26**, 281 ; *J.*, 1921, 699A.
[62] *Forsch. Geb. Ing.*, M, [1], 27 ; *J.*, 1921, 84A.
[63] *Z. Metallk.*, 1921, **13**, 177 ; *J.*, 1921, 546A.
[64] *Proc. Roy. Soc.*, 1921, **99A**, 47.

system thus studied is very complex, and the eutectic is of an unusual kind. Among other alloys, Hanzsel[65] mentions one containing 70% zinc and the rest aluminium as having been used in Germany to replace brass, but as too brittle to be very valuable. Some of the alloys richer in zinc could be improved by hot extrusion. One of the alloys containing copper and aluminium has been largely manufactured under the name of Tenax metal, mainly in the extruded state. Its mechanical properties and behaviour towards corroding agents are described by W. Schulte.[66]

Bearing Metals.

A large work on these alloys has been published by J. Czochralski, and some chapters of this have appeared separately.[67] The chief effort in recent years has been to find suitable substitutes for the costly tin, and alloys with a lead basis have found most application. Barium has been widely used as a hardening element for lead in place of tin and antimony, and the lead-barium alloys have the closest resemblance in structure to those with a tin basis. The hard compound has the formula $BaPb_2$, and small additions of sodium are found by J. Czochralski and E. Rassow[68] to improve the structure. Calcium is rather inferior to barium as a hardening element, but is used in the same way. It is claimed that lead hardened by barium is even superior to red bronze for heavy machine bearings, and decidedly superior to all alloys with a tin basis. The behaviour of various bearing alloys on re-melting is described by B. Simmersbach,[69] whilst J. R. Freeman and R. W. Woodward[70] have determined the properties of several such alloys at high temperatures. The newer alloys, with barium or other less common metals, were not tested, but alloys with a tin basis were found to be considerably better than those rich in lead when loaded at temperatures approaching 100° C. Moderate additions of lead to tin alloys are without much harmful effect.

Amongst miscellaneous alloys, nichrome has now assumed great importance, on account of its remarkable resistance to high temperatures, and of its useful electrical properties. The inferior quality of much of the metal manufactured during the last few years is traced by M. von Schwarz[71] to the replacement of a large part of the nickel by iron for the sake of cheapness, such wire oxidising rapidly.

[65] *Z. Metallk.*, 1921, **13**, 209 ; *J.*, 1921, 546A.
[66] *Giesserei-Zeit.*, 1921, **18**, 258, 268, 278 ; *J.*, 1921, 774A.
[67] *Z. Metallk.*, 1920, **12**, 371 ; *J.*, 1921, 306A.
[68] *Ibid.*, 1920, **12**, 337.
[69] *Chem.-Zeit.*, 1921, **45**, 216 ; *J.*, 1921, 222A.
[70] *U.S. Bureau Stand., Tech. Paper* 188 (1921).
[71] *Z. Metallk.*, 1921, **13**, 125 ; *J.*, 1921, 352A.

The metallurgy of ductile tungsten presents many interesting features, and an article by A. O.[72] contains some additional details of the methods now practised. The brittle rod of tungsten is sometimes enclosed in a shell of copper, iron, or nickel, so that it may be drawn at a red heat, the coating being afterwards removed by chemical means or by electric sputtering. In another process the tungsten is mechanically mixed with nickel, and the compound wire then drawn, an alloy being formed, from which the added metal is subsequently removed by volatilisation in a vacuum. The swaging of sintered rods is a simpler process, but an interesting detail is the pointing of the wires for further drawing. Filing and grinding have proved to be impracticable, and two methods have been adopted, one of which consists in oxidising the end of the wire in a gas flame, a conical shell of oxide being obtained, which is then detached, whilst the other makes use of an electric discharge between the point of the wire and another electrode in dilute sulphuric acid, using a high current density. Colloidal graphite, tungsten sulphide, and oil rendered viscous by cooling in carbon dioxide and ether, are used as lubricants during drawing. The final reduction in thickness, when the diameter is so small that the preparation of the diamond dies is difficult, is effected electrolytically, the wire being first made the anode in an alkaline solution, which causes the formation of a layer of oxide, and then the cathode in an acid bath, so that the oxide is dissolved. It is evident that the production of such thin wires of a highly refractory metal introduces quite new problems into metallurgy, which have to be solved by entirely novel methods, of great scientific interest. The production of tungsten lamp filaments is one of the triumphs of recent metallurgical science.

Corrosion and Protection of Metals.

There have been no extensive researches on corrosion during the year, but many workers have examined minor questions and obtained results of some interest. The black deposit formed on aluminium when vessels of that metal are used continuously for heating water has been examined by J. Czochralski,[73] who finds that the blackening occurs with all commercial grades of aluminium, that the deposit contains about three times as much iron and silicon as the metal from which it is formed, and that it is only in alkaline waters that the action takes place. Under the microscope it is seen that the aluminium-iron compound is the first to be attacked, and that the iron is then re-deposited at some distance. In strongly alkaline waters, the attack is more rapid, but the deposit does not adhere.

[72] *Metall u. Erz*, 1920, **17**, 449.

[73] *Z. Metallk.*, 1920, **12**, 430; *J.*, 1921, 351A.

J. C. Thresh [74] shows that water alone is without action on lead, and that the corrosion observed is due to the action of dissolved oxygen, forming a soluble hydroxide, which either passes into a colloidal condition, or combines with other dissolved substances to form soluble or insoluble lead salts. Some salts are deposited on the metal in such a way as to protect against further corrosion, whilst others are continuously removed. The curious variations in the resistance of sheet lead to attack by sulphuric acid when used in chemical plant have been studied by W. G. McKellar,[75] according to whom the physical condition of the sheets is of great importance, intercrystalline brittleness being sometimes observed. It has not been found possible to establish a relation between the chemical composition and the resistance to acid, and the supposed protective value of copper as a constituent has not been confirmed. Inclusions of lead oxide cause rapid corrosion.

The controversy as to the nature of the erosion of marine propellers of non-ferrous alloys has been renewed. O. Silberrad[76] holds that the action is a mechanical one, and can be imitated by the action of a jet of water impinging on the propeller with a high velocity, and that the beta brasses are more resistant than those which are made up of two phases. On the other hand, W. Ramsay [77] maintains that the action is electrochemical. The experiments of Carpenter and others have, however, made it clear that cavitation is responsible for the effect, which is only observed at very high speeds, and that erosion is therefore a special type of decay, mechanical rather than chemical in its nature.

Experiments to test the comparative value of different metallic coatings for preservation against rusting and other forms of corrosion have been made by W. Lange.[78] Hot-dipping in molten tin or zinc, cold electrolytic deposition of zinc, tin, or lead, spraying with metal by the Schoop process, and deposition from vapour, as in Sherardising, have been systematically compared, with results which are interesting in themselves, but do not lead to definite general conclusions. It is evident that coatings of very unequal value may be obtained by the same process by making slight alterations in the conditions. The method of calorisation is described by L. Guillet.[79] Iron, steel, copper, bronzes, and nickel may be protected in this way. The objects to be coated are heated to about 850° C. in a revolving oven in a mixture composed of aluminium 49%, alumina 49%, and aluminium chloride 2%. Any machining must be performed before the metal is coated. A

[74] *Analyst*, 1921, **46**, 270; *J.*, 1921, 627A.

[75] *J.*, 1921, 137T.

[76] *J.*, 1921, 38T.

[77] *J.*, 1921, 65T.

[78] *Z. Metallk.*, 1921, **13**, 161, 267; *J.*, 1921, 547A.

[79] *Rev. Mét.*, 1921, **18**, 285.

superficial layer of an alloy is formed, and this is protected by a firmly adherent layer of alumina. The special advantage of this coating lies in its high resistance to oxidation when heated. At temperatures of 700°–800° C. the metal usually lasts from 5 to 20 times as long as if it were uncoated.

The Schoop process of metal spraying has now been in existence for about ten years, and has been greatly improved during that time, so that it competes successfully with both hot galvanising and electrolytic processes for the protection of metal. A convenient form of the process is described by N. Meurer.[80] The small objects to be treated are placed in a revolving drum, in which they can be exposed, first to a sand blast in order to prepare the surface, and then to the metal spray from an oxy-hydrogen apparatus. Several modifications of the machine are described, suitable for spraying with different metals. The application of zinc is continued for 8–10 minutes, the objects being heated to 80°–100° C., whilst lead must be so applied as to form a much thicker layer, and about 30 minutes is required. For aluminium, 50 to 75 minutes at a temperature of 150°–200° C. is necessary. Thicker layers must be applied if the surface is to be ground or polished after coating. Copper may be applied, but in this case the coating is dark in colour, and must be brightened by dipping in nitric acid.

Season-Cracking.

The subject of season-cracking and of similar failures in metals has engaged the attention of many metallurgists during the past year. At the Spring meeting of the Institute of Metals, an important paper on the season-cracking of brass was contributed by H. Moore, S. Beckinsale, and C. E. Mallinson,[81] the conclusions reached being that such failures are always due to stresses, mostly internal, and are usually connected with corrosion by certain specific agents, of which mercury and ammonia are the most important. The cracks are intercrystalline, and start where the metal is in tension. Annealing at a temperature so low as to cause no appreciable loss of hardness will completely remove the dangerous stresses. The Faraday Society devoted a meeting to the subject, and the papers have been published in volume form.[82] One interesting case of intercrystalline failure there described is that of lead sheathing of cables, investigated by L. Archbutt. This is a time effect, usually connected with a weak crystalline structure. Moore and his colleagues dealt with the process of low-temperature annealing, and O. W. Ellis showed how successful

[80] *Metall u. Erz*, 1921, **18**, 384; *Elektrochem. Zeits.*, 1921, **27**, 102, 114; **28**, 5, 13; *J.*, 1921, 852A.

[81] *J. Inst. Metals*, 1921, **25**, 35; *J.*, 1921, 221A.

[82] *Trans. Faraday Soc.*, 1921, **17** [1]; *cf. J.*, 1922, 105A.

this treatment had been in removing trouble caused by the cracking of brass rods at Woolwich Arsenal during the war. A large group of papers was devoted to steel, but the whole volume should be studied by those who are interested. The facts have been established very clearly, but doubt still exists as to the explanation of them. Rosenhain's theory of amorphous layers between the crystals holds the field, as no other has yet succeeded in explaining more than a small number of the facts, but its acceptance is theoretically difficult. One question naturally asked by engineers is, why do not all metals fail even under small stresses if continued during a sufficiently long time? The study of strained metals by means of X-rays may throw light on the problem, and this has been undertaken by S. Nishikawa and G. Asahara,[83] and by E. C. Bain and Z. Jeffries,[84] the results not being as yet conclusive, although useful indications have been obtained.

It would be improper to conclude even such an imperfect record of the year's work in non-ferrous metallurgy as this without a mention of the scientific investigations bearing on the formation of new crystal grains during the annealing of metals and alloys after cold-working. The paper on the recrystallisation of aluminium sheet by H. C. H. Carpenter and C. F. Elam[85] showed, more clearly than ever before, the origin of the new crystals at the boundaries of the old, the authors having overcome the practical difficulties of obtaining clearly etched structures in worked metal. The results were confirmed by a few observations on brass and on an alloy of aluminium and zinc. The conclusion was reached that the origin of the new crystals is always at a boundary between crystals or between twin lamellæ. There are other observations which tend to show that all metals do not behave alike, and F. Adcock[86] has succeeded in etching 80 : 20 cupro-nickel in the worked state so clearly that the boundaries can be traced quite distinctly even after large reductions in the rolls. He uses electrolytic methods of etching. A most remarkable advance has since been made by Carpenter and Elam.[87] By straining very slightly before annealing, these authors have succeeded in producing such excessive grain growth that full-sized tensile test pieces come to consist of a single crystal. As might be expected, these specimens no longer exhibit the quasi-isotropy of ordinary metallic masses, but become deformed in a manner depending entirely on the orientation of the crystal to the applied force, with most remarkable results. The importance of this development cannot be over-rated, as it is essential to the full

[83] *Phys. Rev.*, 1920, **15**, 38; *J.*, 1921, 515A.
[84] *Chem. and Met. Eng.*, 1921, **25**, 775; *J.*, 1921, 852A.
[85] *J. Inst. Metals*, 1921, **25**, 259; *J.*, 1921, 222A.
[86] *Ibid.*, 1921, **26**, 361; *J.*, 1921, 702A.
[87] *Proc. Roy. Soc.*, 1921, **100A**, 329; *J.*, 1922, 17A.

knowledge of the plasticity of metals that the properties of isolated crystals should be known, and practical difficulties in the way of testing such crystals have hitherto proved an insurmountable obstacle. Equally interesting results were obtained from such test pieces as consisted of two or three crystals, and light may thus be thrown on the still unsolved problem of the nature of the intercrystalline boundary.

ELECTRO-CHEMICAL AND ELECTRO-METALLURGICAL INDUSTRIES.

By J. N. Pring, D.Sc.,

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The electro-chemical and electro-metallurgical industries, in common with other industries, have suffered from the continued industrial depression which has extended throughout the year. In this country blast furnaces and steel plants have been forced to stand idle generally, and though some signs of revival are now apparent, there has been little or no demand for the high-class ingot steels and alloys which were made in the electric furnace at Sheffield and elsewhere during the war. In addition to the effects of the shortage of coal resulting from the dispute which extended over a portion of the year, a serious curtailment in power supplies has also been experienced in water-power centres, as in the French Alps, Italy, Switzerland, and Scandinavia, from the prolonged drought. These factors have led to a considerable reduction in the output of electro-chemical products, underselling, and a fall in prices. In the case of some of the main products the prices obtaining at the beginning and end of the year are as follows[1] :—

	Beginning 1921.	End 1921.
Calcium carbide	£20 per ton	£15 per ton
Aluminium	£150	£110
Ferro-silicon, 45%	£18	£13
Ferro-chromium, 6 8% C	£37	£25 10
Ferro-chromium, 1% C	£106	£91
Ferro-tungsten, 80%	2/6 per lb.	1/5 per lb.
Ferro-manganese	£22 per ton	£14 per ton
Ferro-molybdenum, 70%	7/6 per lb.	6/9 per lb.
Ferro-phosphorus, 20%	£48 per ton	£18 per ton
Ferro-vanadium, 35%	32/- per lb.	20/6 per lb.

[1] *J. du Four Elec.*, 1922, **31**, 1.

The slump in the market for ferro-alloys which have a large outlet in armour-plate manufacture has been accentuated further by the decisions of the Washington Conference, and, particularly in the case of ferro-tungsten, through exports from Germany. In the case of calcium carbide production large works in Scandinavia, such as those at Odda, have suspended operations, and Swiss works have diverted power supplies to traction and lighting on account of the importation of carbide from countries with depreciated exchanges.

With regard to electro-metallurgical practice, the main advance which has been made during the year is in the direction of continuing to apply electric furnaces to deal with wider ranges of temperature than were formerly considered possible. There has been an increased demand for electric furnaces to operate up to 2000° F. (1100° C.) to be used for a great variety of heat-treating operations. The main advantages which are thus obtained are the rapidity with which the temperature can be raised, and the ease with which uniform heating can be ensured throughout the charge and the temperature controlled automatically. The chief applications of these furnaces have been in the annealing and hardening of structural steel, the melting of non-ferrous metals and preparation of alloys, the baking of vitreous enamel, and the annealing of glass. In some localities it has further been found practicable and economical to utilise electric energy for generating steam.

Developments in Power Generation.

The operation of electro-chemical and electro-metallurgical processes is largely conditioned by the availability of large amounts of power. The progress which is being made in the construction of large steam-power stations continues to counteract the disabilities that the lack of large water powers have imposed on this country in the past. In large industrial centres in Great Britain electric power is supplied at a rate which enables various electro-chemical processes to compete with works abroad and with older fuel-heated processes in this country. In the North-East Coast District, including Northumberland and Durham, the Newcastle-on-Tyne Electrical Supply Co. and other interlinked companies were, at the beginning of 1921, supplying a total of 480,000 h.p.[2] The decreased demands due to cessation of work in munitions factories and other war industries were, in spite of the trade depression, made good by industrial demands.

With reference to water powers, the position in this country is discussed at length in the Final Report of the Water Power Resources

[2] *Electrician*, 1921, **87**, 258, 286.

Committee of the Board of Trade, which has recently appeared.[3] It is concluded by this Committee that in Great Britain some 210,000 k.w. could be developed continuously from potential water powers at an economic rate. This output is about 40% of the total units generated during the year 1917-18 in the 410 steam power stations for electricity supply and for electric railways and tramways in Great Britain, and represents the equivalent of some 3,000,000 tons of coal consumed in power production. This estimate does not take into account the power to be derived from potential water resources, for which the Committee has insufficient data to enable estimates to be deduced. As for Ireland, the Sub-Committee estimated an available continuous potential water power of 113,000 kw. The Committee reiterates its previous recommendation with regard to tidal power schemes, *viz.*, that this subject should be specially studied by a technical commission, with particular reference to the Severn Estuary, in connexion with which a considerable amount of information has already been accumulated, and which is believed to present the best prospect of success in comparison with other tidal schemes. Scotland is shown by the Commission to offer a number of comparatively large schemes. Nine of the more immediately promising of those examined have an average output ranging from 7000 to 40,000 continuous h.p., and an aggregate capacity of 183,000 h.p. In North Wales a number of attractive schemes are available, though these are in general more expensive than those in Scotland. In England there are no schemes of any large individual magnitude except, possibly, around Dartmoor. It is expected that, in the near future, the Lochaber scheme will be developed whereby 72,000 continuous h.p. will be generated and employed for the manufacture of aluminium.

In a Presidential Address to the Engineering Section of the British Association,[4] A. H. Gibson gives statistics of the potential and developed water power in different countries. The available water power of the world is shown to be of the order of 200,000,000 h.p., of which approximately 25 millions is at present developed or in course of development. An increasing proportion of water power is being used for electro-chemical and electro-metallurgical processes. In Norway, for instance, the electro-chemical industry in 1918 absorbed 770,000 h.p., or approximately 75% of the total output. Of this some 400,000 h.p. was utilised in nitrogen fixation alone. According to H. A. Winne,[5] the total installed kv.-a. capacity of electric steel furnaces in United States in 1921 amounted to 400,000 h.p.

[3] H. M. Stationery Office, London, 1921 ; *J.*, 1921, 438R.

[4] "Notes on Water Power Development," Report of 1921 Meeting, pp. 110-124.

[5] *Gen. Elec. Rev.*, 1921, **24**, 510.

Recent progress in hydro-electric development is mainly noticeable in the increase of the size of individual turbo-generator units. In the Queenston-Cheppawa project at Niagara Falls, units having a maximum capacity of 55,000 h.p. under a head of 305 ft. are, at the present time, being installed. In the case of low-head turbines, important progress is being made in increasing the speed of rotation, the low value of which has so far offered a serious limitation with these turbines.

Tidal Power.—It is pointed out by Prof. Gibson that the power obtainable from the suggested Severn installation alone for a period of 8 hours daily throughout the year, would be of the order of 450,000 h.p. The only practicable means of utilising tidal energy on any large scale would appear to involve the provision of one or more dams, impounding the water in tidal basins, and using it to drive turbines. The intermittent supply thus obtained would involve the adoption of some form of storage system or the operation of intermittently-worked electro-chemical processes.

In France, a special commission has been appointed by the Ministry of Public Works to consider the development of tidal power, and it has been decided to erect a 3000-kw. experimental plant on the coast of Brittany.

A detailed description, with illustrations and diagrams, of water powers from geographical, engineering, and industrial aspects has been given by F. Robinson.[6] This discussion includes an outline of all the main water powers which have been developed or are under consideration in different countries.

G. Fox and F. H. Willcox[7] discuss recent developments in the generation of power from blast furnace gas. The technique of the handling and cleaning of the gas is described, numerous recent installations are cited, and the developments in design are summarised.

Laboratory and General Electric Furnaces.

E. Griffiths[8] gives a detailed description of the different types of laboratory and industrial furnaces at present in use. These include: (1) wire or ribbon-wound tubular furnaces, (2) graphite spiral furnaces, (3) carbon tube furnaces, (4) tungsten and iridium tube furnaces, (5) zirconia-yttria tube furnaces, (6) granular resistance furnaces, (7) induction furnaces for low and high frequency, (8) arc furnaces, (9) cathode-ray furnaces.

F. Rawlinson[9] gives a general outline of the principles of electric smelting furnace operation, with diagrams of different types.

[6] *Beama*, 1921, **9**, 224, 351, 451.
[7] *Power*, 1921, **54**, 706.
[8] *Beama*, 1921, **9**, 12, 145, 254.
[9] *Beama*, 1921, **8**, 14, 140.

M. Gillot and M. V. Guillermin[10] give a general discussion on electric furnace operation including current supply and the properties of electrodes and linings.

The Tagliaferri furnace,[11] which has been recently introduced, is of the arc type for use with three-phase current. The arcs are formed between vertically-suspended electrodes and either the surface of the bath or auxilliary side electrodes. The voltage between each phase is 100 to 130. Units have been constructed up to a capacity of 30 tons.

E. F. Northrup[12] describes the design, operation, melting rate, and power input of furnaces using high-frequency inductive heating. Recent progress is outlined and a description given of various types of furnaces in sizes up to 60 kw. The furnaces consist of a cylinder of flattened copper tubing wound edgewise, the inside of which is fitted with a refractory cylinder containing the metal to be heated. Current of a periodicity from 10,000 to 25,000 cycles per second is applied to the cylinder and the heat is generated in the centre by the " eddy " effect.

A new type of induction furnace designed by the General Electric Company[13] employs a primary winding above the bath and in close proximity to the metal. The reactance is thus lowered and the use of a current of normal periodicity made possible in place of the low periodicity of the other types of induction furnaces. In a unit of 2 tons capacity, consuming 250 kw., when melting down scrap, the energy consumption measured at the transformer terminals is 775 kw.-hours per ton of metal formed and the time per heat is 2¾ hrs. An improvement in the refractory lining has enabled over 600 heats to be obtained during a run extending over 3 months.

Electrodes.

According to J. W. Richards[14] the Söderberg electrode is rapidly replacing the older types. In Norway, at one of the metallurgical plants, an electrode of this type carries 1000 amps. At an electric steel plant a tilting Héroult furnace is equipped with these electrodes which are fed in sections 2 metres long. At another plant large aluminium-cased Söderberg electrodes up to 18 inches square have been applied to aluminium cells. The consumption of the electrode in the bauxite bath is very uniform, the end of the electrodes remaining parallel.

[10] *Foundry Trade J.*, 1921, **23**, 535.
[11] *J. du Four Elec.*, 1921, **30**, 53.
[12] *Chem. and Met. Eng.*, 1921, **24**, 1097 ; *J.*, 1921, 220A.
[13] *Iron Age*, 1921, **108**, 344.
[14] *Chem. and Met. Eng.*, 1921, **25**, 687.

Electrode Regulators.

An improved type of automatic electrode regulator has been introduced by the General Electric Co.,[15] by which a notably even load is obtained in the power circuit when operating arc furnaces. A further new type of regulator which responds rapidly to fluctuations in the resistance and thus offers a steady load to the power supply, is that recently applied by Mylius.[16]

ELECTRIC SMELTING OF IRON ORE.

Recent developments of the works at Domnarfvet, in Sweden, are described by G. De Geer.[17] During the war it was necessary to abandon the manufacture of coke pig-iron on account of the shortage of fuel. At the present time six electric pig-iron furnaces are built or in course of construction, five of the Elektrometall and one of the Helfenstein type with a total capacity of 31,000 kw. Electric steel furnaces are also being installed for melting cold scrap. Experiments made to dispense with charcoal have shown that good results are obtained with mixtures of 50% of coke and 50% of charcoal. With a higher proportion of coke the output decreased and results obtained were poor. The difficulty with coke in iron ore furnaces is mainly due to its graphitisation, which leads to too great a fall in resistance and is found to take place to a greater degree when the charge descends too slowly. It is considered that this defect should be obviated by a suitable modification in the design of the furnaces, which have hitherto been constructed mainly for use with charcoal.

J. Herlenius[18] gives a brief description of the constructional details of the Swedish electric pig-iron furnaces, and the results of its use in commercial practice are summarised. Units range in size from 2200 to 8000 kw. The methods of starting, operation, electrodes, and gas circulation are discussed. In high-powered furnaces sulphur can be successfully eliminated when producing grey iron.

Noteworthy plants for the electrical smelting of a local hæmatite ore and for the electrical manufacture of steel are being installed in Brazil to be operated from a water power.[19] The Elektrometall type of electric pig-iron furnace is being employed with the modification that the diameter and height of the shaft will be reduced, as the Brazilian charcoal is very much denser than that made from the northern conifers. The pig-iron will be treated first in a Bessemer converter and then finally refined in a 6-ton Ludlum

[15] *Gen. Elec. Rev.*, 1921, **24**, 833; 1922, **25**, 19.
[16] *Electrician*, 1921, **87**, 517.
[17] *Chem. and Met. Eng.*, 1921, **24**, 429.
[18] *Ibid.*, 1921, **24**, 108.
[19] *Ibid.*, 1921, **25**, 1057.

electric steel furnace. This furnace is operated by three-phase current and has three electrodes set in a row over an oval-shaped accessible hearth with doors at each end and a removable roof.

In the Belgian Congo electric smelting of a local iron ore is being undertaken at the Lubudi Falls, which yields 16,000 h.p. continuously.[20]

A works has been established by the "Akt. Norges Stal" Co., near Trondhjem,[21] for the direct reduction of iron ore in order to obtain iron of similar quality to electrolytic iron. Reduction is effected in a shaft house by gas, which first passes through a high-tension electric furnace similar to the Birkeland furnace. It is proposed to construct a unit of 3000 kw.

At Aoste,[22] a works is in course of construction by the Société Ansaldo for the electric smelting of the magnetic iron ore deposits of the Val de Cogne. Two electric shaft furnaces have been installed. Steel, ferro-alloys, and electrodes will also be manufactured here.

Electric Steel Furnaces.

J. B. C. Kershaw[23] discusses the position of electric steel and recent developments in the mechanism of the Héroult and the Grönwall or "Elektrometall" types of furnaces. A description is given of the Russ electric arc furnaces as designed in Germany and characterised by possessing a modified type of electrode. In Great Britain the small furnace of 5 to 7 tons has been found the most useful and economical since the usual application has been for the melting and refining of cold scrap, while in America, Germany and France, the custom has been to use electric furnaces, of 25 tons or more capacity, for the final refining of molten metal from the Bessemer converter or open-hearth.

Two 40-ton Héroult steel refining furnaces which were brought into operation at the U.S. Naval Ordnance plant, South Charleston, W. Va., in February, 1921,[24] mark a considerable step forward in the electrometallurgy of iron and steel. These furnaces are operated in conjunction with two 75-ton basic open-hearth furnaces using natural gas of 950–1000 B.Th.U., and, after dephosphorising, the molten steel is transferred to the basic-lined electric furnace to be desulphurised, deoxidised, and brought to the final temperature of 1650° C., when the metal is tapped into the ladle. The total metal losses, including slag losses, handling metal, etc. are stated to be as low as ½–1½% in the electric furnace, as compared with 8–12% in the open-hearth furnace. One of the furnaces is fitted

[20] *J. du Four Elec.*, 1921, **30**, 85.
[21] *Ibid.*, 1921, **30**, 141.
[22] *Ibid.*, 1921, **30**, 101.
[23] *Electrician*, 1921, **87**, 636.
[24] J. A. Seede, *Gen. Elec. Rev.*, 1921, **24**, 833 ; 1922, **25**, 19.

with 24-inch carbon electrodes and the other with 14-inch graphite electrodes, thus giving current densities of 46·8 and 137·5 amps. per sq. in. respectively, with the transformer at its maximum output of 21,200 amps. per phase. Each three-phase transformer gives 17,300 amps. per phase with 110 volts between phases, or a total of 3300 kv.-a. By means of tappings in the high-voltage windings, 21,200 amps. per phase can be supplied at 90 volts between each phase.

The Newkirk type of furnace which has been introduced recently contains three suspended graphite electrodes for three-phase current and a metal hearth electrode embedded in the furnace lining and connected to the neutral point of the transformer.[25]

R. Moldenke[26] discusses the relative advantages and costs of refining from cold metal, and by the duplex treatment. A description is given of the conditions for the control of sulphur, manganese, and phosphorus content, the advantages of acid and basic hearths, and the influence of the temperature of tapping.

A. Stansfield[27] gives a classification of electric steel-making furnaces and discusses their general features, relative merits, and the advantages of hearth-electrode arc furnaces.

L. J. Barton[28] describes experiments made with three forms of furnace bottoms, the methods of building bottoms, and experiments with roof and side wall linings.

A method has been devised by J. W. Moffatt[29] for preparing steel direct from ore. The process is adapted for treating low-grade and inferior iron ore. The finely-divided ore is reduced first to a sponge by means of furnace gases and is then smelted in an electric furnace to steel. The power expenditure is stated to be 700–750 kw.-hrs. per ton of steel as compared with 2500 kw.-hrs. in Swedish practice.

Electrolytic Iron.

W. E. Hughes[30] reviews the methods employed in the electro-deposition of iron particularly from sulphate, chloride, and sulphate-chloride solutions. The chloride bath allows of greater current density and is a better conductor than the sulphate solution, but has the disadvantage that a higher temperature of working is necessary whereas the sulphate solution can be worked at ordinary temperatures. The deposited metal oxidises more rapidly with a chloride bath than with a sulphate solution. A slight acidity, especially when using sulphate solutions, improves the conductivity

25 *Iron Age*, 1921, **107**, 691.
26 *Ibid.*, 1921, **107**, 437; *Foundry Trade J.*, 1921, **23**, 221.
27 *Blast Furnace and Steel Plant*, 1921, **9**, 263, 324, 381, 488.
28 *Iron Age*, 1921, **108**, 581.
29 *Ibid.*, 1921, **107**, 1450.
30 *Trans. Amer. Electrochem. Soc.*, 1921, 15; *J.*, 1921, 626A.

and hinders oxidation of the bath. A greater degree of acidity impedes cathode efficiency and causes diminution in the grain size of the deposit, accompanied by increased hardness and brittleness.

A process introduced by F. A. Eustis and C. P. Perin[31] is being applied for the electrolytic extraction of iron from solutions of ore. The electrolyte is ferrous chloride, the anodes are of graphite, current density 50 amps. per sq. foot, and the cathode is a rotating mandrel on which the iron is deposited as a tube, or consists of a travelling belt. Ferric chloride, which is formed in the anode compartment, is used again for leaching the sulphide ore, thus giving a cyclic process. 97% of the iron, and 90% of the sulphur are said to be extracted. The process is being worked commercially at Grenoble for the production of boiler tubes. The metal deposited on the rotating mandrel contains 99·97% Fe, and is afterwards annealed to remove embrittling hydrogen. It is then stripped and used as a boiler tube, either with or without drawing through a die. The current expenditure amounts to ¼ to ⅓ h.p.-year per ton of tubes. The material produced is particularly soft, due partly to the low carbon content (about 0·008%), and can be drawn through a die five times without annealing. The metal is highly resistant against corrosion.

A plant for the preparation of electrolytic iron, giving an output of two tons a day has also been installed by the Western Electric Co., at Hawthorne, Ill., U.S.A. The metal is employed in telephone construction. The electrolyte consists of ferrous sulphate and chloride and ammonium sulphate. The anodes are of mild steel and the cathodes of polished sheets of steel from which the deposit is stripped when it has reached a thickness of ⅛ to ¼ inch; the current density is about 12 amps. per sq. foot.

Ferro-Alloys.

Among the ferro-alloys which have recently acquired considerable importance may be mentioned ferro-silicon in its application to the production of special grades of sheet steel that are now used in the manufacture of motors, generators, and transformers. Of the other ferro-alloys, all are used in the manufacture of high-grade alloy steels and several have special uses, such as ferro-chromium in the manufacture of stainless and corrosion-resisting steels, ferro-vanadium in spring manufacture, and both alloys, together with ferro-tungsten, ferro-molybdenum, and ferro-uranium, in the production of high-speed steels.[32]

In the manufacture of ferro-manganese, according to R. M. Keeney,[33] the electric furnace gives, for the same grade of ore,

[31] *Iron Age*, 1922, **109**, 22; *Chem. and Met. Eng.*, 1921, **25**, 689; 1922, **26**, 128.

[32] J. A. Seede, *Gen. Elec. Rev.*, 1921, **24**, 522.

[33] *Min. and Met.*, 1921, No. 170, 31; *J.*, 1921, 304A.

at least 5% greater recovery than the blast furnace, and at the present price of coke, fuel and power costs balance. Among the general operating difficulties encountered with the electric furnace, formation of carbide is the most serious. This tendency is found to be modified by the use of lignite as a reducing agent in preference to anthracite or bituminous coal, and also by not attempting to produce a slag containing less than 12% of manganese. The manufacture of ferro-manganese containing 73·6% Mn has been conducted in the United States in an electric furnace of 1100 kw. capacity by smelting ore containing 34·8% Mn and 13·2% SiO_2 with an average power consumption of 4990 kw.-hrs. per gross ton. The electrode consumption has been reduced to 141 lb. per ton of metal. A new type of furnace for the manufacture of ferro-tungsten has been introduced by J. C. Dailey.[34] This consists of a rectangular container open at the top with the hearth only of refractory bricks. Two cylindrical electrodes are used which, together with the hearth, are operated by two-phase current. 817 kg. of ferro-tungsten with 75% W is given per 30 hours, representing 3·5 kw.-hrs. per kg. of tungsten. Acid working (by using silicious slag) gives better yields as the tungsten has less tendency to pass into the slag.

Electric Smelting of Zinc Ores.

In an extension of the electric smelting plants at Trölhattan, in Sweden, and Sarpsborg, in Norway, a new installation is being built at Glomfjord, which will have a capacity for smelting 60,000 tons of ore per annum.[35]

The system now generally employed in Scandinavia consists of resistance furnaces run at high temperatures in place of the arc type, the lead being completely volatilised together with the zinc, and condensed as a powder by rapidly cooling and finally refined by redistillation in an electric arc furnace. The works at Trölhattan is stated to employ 13,000 h.p., the energy expenditure amounting to 1·2 kw.-yrs. per ton of zinc from roasted blende containing 33% Zn. In a process of Thoraldsen in operation at Bergen, using ore with 50% of zinc, and a resistance type of furnace, one ton of metal is stated to be produced per 0·46 kw.-yr.[36] An important advantage in electro-thermic smelting is the recovery of the by-products in the form of lead bullion and copper matte.

J. W. Richards[37] announces an invention of Cornelius which is in operation for conglomerating blue zinc powder by rubbing. This product, which contains 20% Zn, is then redistilled.

[34] *J. du Four Elec.*, 1921, **30**, 105.

[35] W. R. Ingalls, *Trans. Amer. Electrochem. Soc.*, 1921, 165.

[36] *J. du Four Elec.*, 1921, **30**, 113.

[37] *Trans. Amer. Electrochem. Soc.*, 1921; *cf.* E.P. 170,026; *J.*, 1921, 854A.

The Fulton process, which has been brought into operation at East St. Louis,[38] consists in mixing the zinc ore with coke and forming into briquettes. These are given a preliminary heating by means of oil burners, the oxide is reduced, leaving a skeleton mass of the original form of the briquettes. The material is then built up to form the resister of an electric furnace and the zinc distilled by electrical heating and condensed.

Electrolytic Zinc.

The economy which has been obtained with electrolytic zinc extraction at Great Falls, Trail, and Risdon, in connexion with low-grade and complex ores, has been such as to promise its application to high-grade ores and employing fuel-generated power. It is considered[39] that the amount of fuel consumed in the generation of power required for the liberation of one ton of zinc electrolytically will be no greater than that needed in a modern retort plant for the reduction and distillation of this amount of metal.

Advantages secured by the electrical method in comparison with the retort process include the extraction of a higher percentage of metal; the possibility of treating fines, which are necessarily obtained in a concentration process, and lower grade concentrates; the presence of lead and iron in the ore is much less detrimental; a metal of higher purity is obtained; the labour required is only about one-third.

According to W. R. Ingalls,[40] the electrolytic process produces a high-grade zinc at less cost per ton of ore than in the electrothermic method. The limitations of the electrolytic process, however, are that it must be conducted on a large scale and the capital cost per unit of capacity is greater than that of the ordinary distillation plant. Experimental work now proceeding at Anaconda and Great Falls is being devoted to the reduction of losses of insoluble zinc by more careful control of roasting and to improve the extraction by better design of leaching plant and flowsheet.

A process of Tainton and Pring,[41] which has been brought into operation at Martinez, California, is characterised by the use of a high current density, amounting to 100 amps. per sq. foot of cathode, a high concentration of free sulphuric acid, which may amount to 27%, and the possibility of working in presence of metallic impurities such as arsenic and cobalt. The electrolyte, prepared by leaching the roasted ore, and adding spent electrolyte, contains initially 70 grams of zinc per litre. This is circulated through the cells until the zinc falls to 30 g. per litre and is then applied for the

[38] *J. du Four Elec.*, 1921, **30**, 106.

[39] F. Laist, *Chem. and Met. Eng.*, 1921, **25**, 754.

[40] *Trans. Amer. Electrochem. Soc.*, 1921, 165.

[41] *Trans. Amer. Inst. Min. Met. Eng.*, 1921, No. 1073, 52.

leaching of fresh ore. The average current efficiency obtained is 89% and the average voltage 4 volts per cell. The spacing of the electrodes is 1$\frac{3}{16}$ in. from the face of the lead anode to the face of the cathode. One pound of zinc requires 1·77 kw.-hrs. in electrical energy delivered to the cells. Comparatively even and smooth deposits are obtained up to a thickness of $\frac{1}{4}$ in.

An electrolytic process has been operated at Swansea,[42] whereby a metal containing 99·95% of zinc is produced. Low-grade ore is roasted and the sulphur dioxide applied to the manufacture of sulphuric acid. Electrolysis is conducted at a current density of 3 amps. per sq. dm., and a voltage of 3·5, and proceeds for two days. An energy efficiency of 90% is obtained. The anode used is of lead and the cathode of aluminium. The power expenditure is 4000 kw.-hrs. per ton of zinc.

The electrolytic zinc plant in operation at Risdon, near Hobart, Tasmania, for treating Broken Hill deposits, is designed for the annual production of 20,000–25,000 tons of zinc. In August, 1922 the works will be in full operation, producing 50,000–60,000 tons of refined metal per annum.[43] Water power has been developed by the Tasmanian Government at a cost corresponding to £2 per h.p.-yr.

A process for the electrolytic extraction of zinc which is in operation in Japan is described by M. Namba.[44]

Electric Furnaces for Heat Treatment of Metals.

In a number of recent designs furnaces have been specially adapted to the treatment of sheets, steel chains, automobile parts, axles, bolts and nuts and small parts for aeroplanes as well as non-ferrous and other products.

Electric furnaces for the treatment of brass and bronze developed very largely, especially in America, as a result of the pressure of war demands. An advantage obtained by them is the ability to work with a neutral or reducing atmosphere over the bath and thus prevent oxidation losses.

The following types of furnaces are now in successful use[45]:— (1) The direct arc furnace of which the Snyder is the only representative. (2) The indirect arc furnace of which the Rennerfelt and Detroit are the most successful examples. (3) The vertical ring induction furnace of which the Ajax-Wyatt is the best known and most successful. (4) The granular resistance furnace of which the Baily is the only example.

[42] *J. du Four Elec.*, 1921, **30**, 16.

[43] *J.*, 1921, 48R.

[44] *J.*, 1921, 279T.

[45] J. B. C. Kershaw, *Engineer*, 1921, **131**, 48.

The Ajax-Wyatt[46] furnace, which is of the induction type combined with the "pinch-effect" phenomenon first studied by Hering, is reported to be the most efficient as regards use of power and the lowest in running costs, but possesses the disadvantages of requiring to be charged with molten metal and of not being adapted for intermittent use. Further, no refractory lining has been discovered that will withstand the action of alloys containing over 3% of lead. The Baily furnace is the type of which there are the largest number in operation in the U.S.A.

The Snyder type is particularly suited for use with mechanical charging, and has a large output with a low power consumption, but is only suitable for the pure bronzes or similar alloys containing 5% or less of zinc.

The Rennerfelt or any other stationary or indirect arc furnace is stated to be the most applicable to alloys low in zinc, and is being used in the United States for melting cupro-nickel, bronze, and silver.

The Detroit, or rocking type of indirect arc furnace is applicable to alloys of any zinc content, gives a low power consumption and can be mechanically charged. Data in reference to the different types of furnaces in this connexion are given in the following table:—

Type of furnace.	Power reqd., kw.	Charge of metal in lb.	Output per day in tons.		Power consumption in kw-hrs. per ton.
			10 hrs.	24 hrs.	
1. Ajax-Wyatt (yellow brass)	30 60	300 600	1 to 1½ 2½ to 3	3 to 3½ 6 to 7	325 275
2. Baily (yellow and red brass)	105	800 to 1500	2½ to 3½	6 to 10	475
3. Snyder (bronze)	100 300	600 2000	1¾ —	— 12 to 18	380 —
4. Rennerfelt (red brass and bronze and bearing metal)	100 125 300	500 1000 2000	1½ 2 to 2½ —	— 7 to 10 10 to 16	475 400 —
5. Detroit rocking (yellow and red brass)	40 225 300	125 1300 2000	¾ 3½ 6 to 7	— 8½ 16 to 20	400 332 287

Nos. 3, 4, and 5 use from 2½ lb. to 6 lb. of graphite electrodes per ton of metal charged.

[46] G. H. Clamer, *J. Amer. Inst. Elec. Eng.*, 1920, **39**, 1042.

It will be noted that there is a wide range of power consumption, and that the efficiency of each type of furnace in this respect increases with the size.

A further type of resistance furnace has been recently introduced by the General Electric Company.[47] Heating is effected by means of heavy metallic windings supported in refractory insulators on the inner walls of the furnace chamber. The pitch and length of the ribbon convolutions can be made so as to concentrate or distribute the heating effect as desired. This furnace has been applied largely in America for the treatment of gun forgings, 22 units being installed during the war. A large furnace of this type is at present under construction in an ordnance plant of the U.S. Government, having dimensions of 8 to 10 feet in diameter by 105 feet deep with a connected load of 2700 kw. Several of these heat-treating furnaces are also in use in other countries, notably Canada, France, Spain, Norway, etc.

According to H. W. Gillett[48] the total number of electric furnaces in operation in the U.S.A. in January, 1921, melting non-ferrous metals was 318, with a total capacity of 42,350 kw. Electric melting is well established on brass and bronze, nickel-chromium, and similar alloys, and to a minor extent for melting aluminium.

A number of new types of muffled arc furnaces have been introduced by the General Electric Co. and supplied for melting brass, bronze, and similar non-ferrous alloys.[49]

H. M. St. John[50] describes the advantages gained by the use of large electrically-heated melting units, with closed melting chambers, which are practically free from oxygen and products of combustion, thus producing a more uniformly high quality of product, with less labour and less metal wastage than have previously been obtainable.

W. J. and S. Green[51] discuss the conditions requisite for producing tool steel in the electric furnace.

A. D. Dauch[52] describes automatically-controlled furnaces used for heat treatment and annealing of various automobile parts. The advantages which are obtained by rotary electric furnaces over the oil-fired type for continuous heat-treating, annealing, and carbonising are also pointed out.[53]

In its application to the melting of silver[54] the electric furnace eliminates the high cost of crucibles and the employment of an ex-

[47] E. F. Cone, *Iron Age*, 1921, **108**, 643.
[48] *Trans. Amer. Electrochem. Soc.*, 1921, 277; *J.*, 1921, 701A.
[49] H. A. Winne, *ibid.*, 1921, 263.
[50] *Ibid.*, 1921, 55.
[51] *Iron Age*, 1921, **108**, 669.
[52] *Forg. Heat Treat.*, 1921, **7**, 525.
[53] *Elec. World*, 1921, **78**, 565.
[54] H. A. de Fries, *Trans. Amer. Electrochem. Soc.*, 1921, 199.

perienced melter, which are essential to gas or oil-fired crucible practice. Further advantages are the high pouring temperature, which can be so readily attained in the case of an electric furnace, and the adjustment that can be made between pouring temperatures of bar silver (1033°–1093° C.), and of rolling mill and casting silver (1223°–1304° C.). A Rennerfelt electric furnace of 10,000 oz. capacity and consuming 100 kv.-a., is in use at the Philadelphia mint for the melting of silver. The power consumption averages 180 kw.-hrs. per ton of metal.

In the melting of nickel silver considerable advantages have been obtained by the use of the electric furnace.[55]

Electric Smelting of Tin Ore.

Furnaces at present in use for the electric smelting of tin ore are the Wile furnace and a type described by H. Krebs.[56] In this method ore and coal are charged into a trough furnace provided with a low charging shaft and brought to a molten condition by means of current introduced through two or more electrodes dipping into the bath. The metal is tapped from the bottom. The tin content of the slag can be reduced as low as 0·3%.

Calcium Carbide.

The manufacture of calcium carbide is stated to show signs of increasing,[57] but is hardly being maintained in countries other than those with a depreciated currency such as Germany, Austria, and Czecho-Slovakia, or else in countries having a large consumption or high tariffs such as France, Italy, Spain, and Canada. England consumes 20,000–30,000 tons of carbide per annum, most of which is imported, half coming from Norway. The two English works are the British Carbide Factories, Ltd., with a capacity for producing 5000 tons per annum, and the British Cellulose and Chemical Manufacturing Co., Ltd., with a capacity of 40,000 tons.* At the latter factory the manufacture of carbide has been suspended since 1920. Power is generated from steam at a reported cost of £10 per h.p.-yr. or £6 per ton of carbide. Under these conditions the process is not at present able to compete with water power from countries abroad, except with tariff protection. Calcium carbide is used by the British Cellulose Co. for the generation of acetylene employed at present in the synthetic preparation of artificial silk, of which the daily output is now about one ton, and the manufacture of celluloid which is making good progress.[58]

Extensive developments have taken place in recent years in the manufacture of acetic acid from calcium carbide through the

[55] F. C. Thompson, *ibid.*, 259.
[56] *Metall u. Erz*, 1921, **18**, 77 ; *J.*, 1921, 305A.
[57] *J. du Four Elec.*, 1921, **30**, 136 ; 1922, **31**, 3.
[58] *J.*, 1921, 224R.

intermediate production of acetylene and acetaldehyde.[59] Large quantities of acetic acid were made in this way during the war period to supplement or replace supplies normally obtained by the distillation of wood. The largest installations for this manufacture were erected at Shawinigan Falls, Canada, in Germany, and by the British Cellulose Co. at Spondon. In this country the manufacture has been abandoned on account of the high price of carbide compared with that of imported acetic acid, but in other countries the synthetic acid can be produced at a price which allows of competition with the wood distillation process. The different processes in use, which vary only in detail, are based on the reaction which takes place when acetylene is passed through a solution of mercuric sulphate in sulphuric acid, thus giving acetaldehyde which is then oxidised to acetic acid by passing together with air or oxygen over a catalyst of manganese acetate.

Calcium Cyanamide.

The cyanamide industry reached enormous dimensions during the war as being one of the most economical methods of preparing ammonia on a large scale. Though its application in this connexion is now in abeyance, it still retains a large and growing outlet as a fertiliser either applied directly or after conversion into other derived compounds.

The advantages and disadvantages of the presence in the final product of calcium chloride and fluoride which are added to the furnace charge to serve as catalysts are discussed by H. Gall.[60] The residual amount of carbide in the cyanamide has been reduced to 0·3%. In applying to agriculture, the method of adding water or oil to the product to overcome the harmful effect of the presence of lime during handling has been abandoned in favour of methods devoted to granulation.

New derivatives prepared from cyanamide include "Ammophos," which consists of a double phosphate of calcium and ammonium, prepared by condensing ammonia in a solution of monocalcium phosphate. Urea is made in Savoy by direct conversion of cyanamide, by suspending in water and exposing to the action of carbon dioxide obtained from the calcining of the original limestone. The free cyanamide which is thus obtained is hydrolysed by the addition of a mineral acid, preferably sulphuric acid.

Refractories for Electric Furnaces and Abrasives.

Experiments made at high temperatures with a number of refractories by R. M. Howe[61] showed that under a pressure of 50 lb. per

[59] *J.*, 1921, 345R.
[60] *J. du Four Elec.*, 1921, **30**, 131.
[61] *J. Inst. Metals*, 1921, **25**, 455.

sq. in., all the materials tested yielded at or below 1650° C., with the exception of carborundum. Silica probably fails by shear at the temperature, being rigid at 1500° C. The specific heats of several materials at 100° and 1000° C. are given, all showing an increase with temperature. Fireclay and electric furnace products are found to be only slightly affected by sudden changes in temperature. Silica, magnesia, and chrome brick must be heated slowly,

SUMMARY OF AVERAGE CROSS-BREAKING STRENGTHS.

	Modulus of rupture, lb. per sq. in.		Ratio. R. at 1350° / R. at 20° C.
	20° C.	1350° C.	
Recrystalised carborundum (Refrax)	2312	2437	1·05
Bonded carborundum—Carbofrax A	2103	2274	1·08
Carbofrax B	2651	2129	0·805
Carbofrax C	2215	1918	0·866
Silica No. 1	608	145	0·228
Silica No. 2	491	178	0·363
Magnesia	1388	136	0·098
Fireclay	665	113	0·170
Bauxite	1315	99	0·075
Chrome	1392	22	0·014

especially at low temperatures, if spalling is to be avoided. After the first heating, however, they are improved in this respect. Silica bricks are found to give good service in roofs and zirconite brick has been largely recommended for electric furnaces on account of its high fusion point, low conductivity, and marked resistance to

fluxes. It is necessary, however, that the zirconite should be purified from iron oxide and other impurities and given a severe heat treatment before use in order to eliminate shrinkage. Carborundum and alundum offer good possibilities for service in roofs, as they have all the qualities of a silica brick with less tendency to spall.

The application of zirconia as a refractory is described by J. C. Thompson.[62] The oxide is obtained from zirconite, the silica being removed by an electric furnace process in which the mineral is heated with the necessary amount of coke to produce silicon carbide which is then separated from the zirconia. The removal of iron can be effected subsequently by treatment of the material with chlorine or phosgene. The refractory properties of zirconia and the factors which limit its use are discussed.

M. L. Hartmann and W. A. Koehler [63] describe measurements made on the cross-breaking strength of specialised refractories with the results as set forth on page 311.

The results of a number of experiments made on the physical and chemical characteristics of carborundum refractories when applied to heat treating furnaces are described by M. L. Hartmann.[64]

The properties of sillimanite, which has the composition Al_2O_3,SiO_2, have been described by A. F. Greaves-Walker.[65] The melting point of this refractory is given as 1816° C.

A new abrasive consisting of tungsten carbide has been applied under the name of "volomite." The compound is said to possess a hardness comparable with that of diamond.[66]

Electrolytic Production of Hydrogen and Oxygen.

The uses of electrolytic hydrogen and oxygen are now extending rapidly mainly at Government aircraft stations and in such applications as metal welding and cutting, hydrogenation of oils, manufacture of incandescent filament lamps, metal brazing, oxy-acetylene welding, smelting work, steel production, synthetic ammonia, and accumulator works. The recent developments which have been made in plant for the production of these gases by electrolysis are described by A. J. Hale.[67] The cells now in use may be classified as the bell type, the bipolar or filter-press type as in the Oerlikon cell, and that devised by the National Oxygen Co. of Chicago, and the diaphragm unit cell as first manufactured by the International Oxygen Co. in 1911, an improved form of which is now made by the Davis-Bourneville Co., N.J.

[62] *Trans. Amer. Electrochem. Soc.*, 1921, 291 ; *J.*, 1921, 768A.

[63] *Ibid.*, 1921, 129 ; *J.*, 1921, 771A.

[64] *Trans. Amer. Soc. Steel Treat.*, 1921, **10**, 601.

[65] *J.*, 1922, 13T.

[66] *J. du Four Elec.*, 1921, **30**, 102.

[67] *J.*, 1921, 122B

In all cases each cell is usually capable of taking 300–600 amps., while the voltage varies in the different types from 2·0 to 2·4 The yield of hydrogen varies from 6·0 to 7·5 cub. ft. per kw.-hr The purity of the hydrogen varies from 99·0 to 99·8%, and that of the oxygen from 97 to 99%.

Electrolytic hydrogen is being applied on a large scale in Norway, for use in the operation of the Claude process of ammonia synthesis.[68] For this purpose the Cumberland Coal Power and Chemical Co. has acquired a controlling interest in the Tysse water-power undertaking in Norway. 145,000 h.p. is at present being generated at this centre, 100,000 h.p. being transmitted to Odda. The cost per h.p.-yr. is stated to be as low as £1, or less than 1-25th of a penny per kw.-hr. An electrolytic hydrogen plant which has been installed has a daily capacity of over 9,000,000 cub. ft.

Electrolytic Copper.

A noteworthy plant for the hydro-metallurgical extraction of copper has been installed at Haut-Katanga in the Congo, for the treatment of a low-grade ore containing 6–7% Cu. The process consists of water leaching, followed by electrolysis of the solution. In consequence of the success obtained with a small unit it is intended to attain an output of 100,000 tons of copper per annum. A water power of 25,000 h.p. is being developed for this process.[69]

Sodium Perborate.

An improved process for the electrolytic preparation of sodium perborate has been devised by the Norwegian firm, Fredriksstad Elektrokemiske Fabriker. A dilute solution of borax, together with sodium cyanide is used as the electrolyte. The presence of sodium cyanide prevents metallic impurities from bringing about the decomposition of the perborate.[70]

Electrolysis of Fused Salts.

Calcium.—The conditions found to be most favourable for the preparation of calcium are described by P. H. Brace.[71] The most successful method is found to be that of Rathenau, in which a stick of calcium is built up on a water-cooled cathode, which is suspended vertically above, and makes contact with the surface of the bath. Two water-cooled graphite plates are used as anodes. The temperature of the bath is controlled by varying the separation and degree of immersion of the anodes. The container is made of Acheson graphite of 12 in. outside diameter and 9 in. depth. A

[68] *J.*, 1921, 424R.
[69] *J. du Four Elec.*, 1922, **31**, 5.
[70] *J.*, 1921, 219R.
[71] *J. Inst. Metals*, 1921, **25**, 153 ; *J.*, 1921, 222A.

voltage of 25 to 30 volts is applied and a current of 400 to 500 amps. The diameter of the sticks is uniform and the quality of the metal such that it can be rolled into thin sheets. The best results are obtained by running the cell with sufficient energy input to keep the charge of electrolyte molten, with only a small portion on the sides and bottom of the graphite container remaining solid. The most suitable electrolyte is fused calcium chloride, which has been completely dehydrated.

Magnesium.—The production of magnesium by the electrolysis of the fused chloride has been developed in Wolverhampton by the Magnesium Co.[72] The method used employs an electrolyte of the fused chloride and a cathode of molten lead. An alloy of lead and magnesium is obtained first and then transferred to a second cell, where it forms the anode with an electrolyte of fused magnesium chloride, while the cathode consists of a large number of steel rods of small diameter immersed for a short distance in the electrolyte. The total energy consumption amounts to 8·5 kw.-hrs. per lb. of metal, giving an energy efficiency of about 40%.

Cerium.—A continuous process has been devised for the production of cerium,[73] in which use is made of an electric furnace with non-conducting walls, a conducting hearth as cathode, while the anode is of the same shape as the hearth so as to maintain a uniform current density throughout the bath. Tapping is made through an orifice on a level with the hearth. In the interval between two tappings, the metal is kept at a pasty consistency in front of the tapping hole, so as not to dissolve in the bath. Shortly before tapping, the temperature is raised by increasing the power or adjusting the electrodes.

Electro-Plating.

Zinc.—A process for zinc plating from a cyanide solution which will operate successfully at very high current densities in mechanical units where the cleaning of the work is often poor is described by C. J. Wernlund.[74] The following composition of the bath is recommended, the weights being expressed in grams per litre :—Zinc cyanide 60, sodium cyanide 52·5, sodium hydroxide 7·5–15, sodium carbonate 30, sodium fluoride 7·5, corn sugar 7·5, gum arabic 1·1. The temperature employed is 40°–50° C., and the voltage 3–5. Very smooth greyish-white deposits are obtained and the bath does not deteriorate on standing.

Lead-Tin Alloys.—A process for the electro-deposition of lead-tin alloys on the interior of air flasks of naval torpedoes that has

[72] *Electrician*, 1922, **88**, 92.

[73] *J. du Four Elec.*, 1921, **30**, 106. ; F.P. 508,973.

[74] *Trans. Amer. Electrochem. Soc.*, 1921, 345 ; *J.*, 1921, 851 A.

been developed at the Bureau of Standards, Washington, is described by W. Blum and H. E. Haring.[75] Use is made of a fluoborate solution from which is deposited an alloy of equal weights of lead and tin which are finer grained than either of the separate metals deposited under similar conditions. The anode consists of an alloy of 50% tin and 50% lead. A current density of about 7 amps. per sq. foot is employed, and deposition continued until a thickness of 0·003–0·006 in. is secured.

Copper-Nickel.—In a process devised by W. Blum,[76] for alternately depositing two metals, it is found that if relatively thin layers of nickel are interposed during the deposition of copper, the deposit has a much higher tensile strength than pure copper deposited under the same conditions. It is shown that this effect is due to the influence of the nickel layers in restraining the growth of the copper crystals. A further advantage gained by this method is that higher current densities can be employed without tree formation. In the case of copper, the tensile strength of the deposited metal is found to increase with increasing current density, in the range between 30 and 90 amps. per sq. foot. This process has been applied in the electrolytic reproduction of engraved plates.

Miscellaneous Electrical Heating Processes.

An electrical heating method has been introduced by the Leefur Co. at Leeds[77] for the hardening and tempering of steel wire and strip. The wire is wound over electrical contacts placed at the ends of a non-metallic tube, through which the wire passes, while its temperature is raised to the required degree by the passage of the current. An inert surrounding atmosphere can be maintained in the tube. After heating, the wire can be led into an oil bath for the purpose of quenching. Wire and strip thus treated are left with a bright finish free from all scale and discoloration, while the cost compares very favourably with that obtained by gas.

Electrical Generation of Steam.

In certain European countries possessing water-power resources scarcity and high price of fuel led to the development and installation of apparatus of several types for the generation of steam by electric energy.[78]

In a type of apparatus described by F. A. Lidbury and F. A. Stamps,[79] a steam generator is designed for use with current at 100 volts. A unit of 250 kw., which generates 750 lb. of steam

[75] *Ibid.*, 1921, 147 ; *J.*, 1921, 774A.
[76] *Ibid.*, 1921, 137 ; *J.*, 1921, 773A.
[77] *Engineering*, 1921, **111**, 76.
[78] *Power*, 1921, **53**, 404, 746.
[79] *Trans. Amer. Electrochem. Soc.*, 1921, 77.

per hour, consists of a vertical steel pipe of 12 in. diam., fitted with a number of other concentric steel pipes perforated to allow of circulation and alternately connected with the two insulated end plates of the cylinder. The current is introduced between these end plates and passes through the water between adjacent tubes, the surfaces of which are separated by an interval of 0·75 in.

According to E. A. Low,[80] at a paper mill in Sweden, there are installed seven 2000-kw. boilers operating at 10,000 volts and a steam pressure of 150 lb. The efficiency obtained is 96%. The current is passed from electrodes directly through the water. Each boiler is fitted with 18 electrodes in six groups so that the capacity can be controlled in steps.

Cement Manufacture.

Electric furnaces have been applied to the preparation of cement at a works in the Alps, where 2000–3000 h.p. has been applied.[81]

[80] *Gen. Elec. Rev.*, 1921, **24**, 515.
[81] *J. du Four Elec.*, 1921, **30**, 73, 81.

OILS, FATS, AND WAXES.

By JOHN ALLAN,

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AN examination of the Board of Trade returns of the imports of oils and oilseeds for the past year would be expected to reveal a considerable reduction in values, but probably the more outstanding feature of the returns is the extraordinary way in which receipts from certain sources of supply have practically ceased whilst others have remained normal or even have increased. The falling off is especially noticeable in the case of imports from India. From this source in the first nine months of the year we received only 27,000 tons of linseed, whereas in 1919 our import of Indian linseed was ten times as great. India's place, in the case of this seed, has been taken by the Argentine, from whence in the same time, no less than 86% of our total import of 369,000 tons has come. The amount of cottonseed received from India is also phenomenally low, but this is in some measure compensated for by an increase of about 25% in our import of Egyptian seed.

An interesting extension of the remarks made in last year's report on the effect on cottonseed oil supply of the intended reduction of the area of planted cotton in America and Egypt is obtained from the figures in the following statements. A commentator on the United States Census Bureau's mid-November report of cottonseed and cottonseed products covering the three months ending October 31st, 1921, says[1]: "an 8,000,000 bale crop of cotton (the estimated output for this year) would produce 400,000 tons of cottonseed oil, which together with the carry-over from last season of close on 100,000 tons would give a supply of 500,000 tons for the season." The Crude Cottonseed Oil Tariff Committee of the Interstate Cottonseed Crushers Association, in a letter addressed to those interested in the United States Cotton Oil Industry, says[2]: "If the domestic consumption of cottonseed oil during the next twelve months (after August 1st) is equivalent only to the preceding twelve months—the recent consumption is much greater than last year—*and none is exported*, there will be a shortage of 72.000 tons

[1] *Cotton Oil Press*, Dec., 1921, p. 22.
[2] *Ibid.*, Dec., 1921, p. 19.

and no carry-over on August 1st, 1922." The reflex action of this position on the European markets for cottonseed and other oils can be readily understood.

Recent events have driven home upon the nations of the world how great is their dependence upon the industries concerned with the production and manufacture of oils and fats, whether this dependence be measured from the point of view of foodstuffs or munitions supplies. It is therefore noteworthy that Governmental interest in these industries has been stimulated so far that departments and associations have been created for the purpose of carrying on fundamental research both in the manufacture and uses of oils and fats.

As an outcome of this interest the Italian Government has founded the R. Stazione Sperimentale per l'Industria degli Olii e dei Grassi, with headquarters in Milan, which, as stated by Prof. Fachini, its director, is to be concerned with the investigation of matters pertaining to the industries occupied with the production, manufacture, and use of mineral and fatty oils, varnishes, etc.

A more recent development is the association of the United States Department of Agriculture with varied interests identified with the industry relative to the chemistry, technology, and economics of oils and fats and especially that of cotton oil milling, the intention being to define and co-ordinate the research of the different bureaux of the Department so that the maximum of national benefit may arise from their work. The programme of work already outlined includes such problems as cultural conditions, constituents of natural oils and refining problems, physiological effects, food values, rancidity, etc.

Continued investigation of food principles, and especially of the vitamin known as fat-soluble A, has emphasised the important bearing which manufacturing and refining processes may have upon the dietetic value of a fatty food. The effect of high temperature and of hydrogenation in destroying this vitamin in fish oils cannot be accepted as a generalisation to be applied to all refining and other processes to which edible oils are subjected since F. G. Hopkins[3] has shown that arachis and palm-kernel oil, in the refined state, still contain the vitamin. The larger amount of this vitamin which occurs in butter-fat is not so readily affected by heat alone as it is by exposure to air, even at low temperatures,[4] and this destruction is still more rapidly brought about by ozone.[5] The effect of diet on the vitamin content of milk and also of body fat is very marked, the various dry foods used in winter having the

[3] *Biochem. J.*, 1920, **14**, 725; *J.*, 1921, 363A.

[4] J. C. Drummond and K. H. Coward, *Biochem. J.*, 1920, **14**, 734; *J.*, 1921, 363A.

[5] S. S. Zilva, *Biochem. J.*, 1920, **14**, 740; *J.*, 1921, 363A.

effect of lowering this very considerably.[6] H. Steenbock[7] and his co-workers have shown that highly-coloured butters and beef fats are usually richer in the vitamin than those low in pigments. The development of colour in the fats is probably influenced by the same articles of diet which affect the vitamin content.

The production of glycerol from sugar by controlled fermentation with ordinary yeast is a process of great interest in view of the continued reduction in the price of sugar. It would now appear, however, that to obtain a high conversion of sugar to glycerol is not the only difficulty to be overcome before the process can be economically satisfactory. Literary references to the process give no indication as to whether the figures representing the yield of glycerol obtained—in some cases over 30% of the sugar consumed[8]—refer to the fermented liquor or to the glycerol in a technically usable form obtained from this liquor. The published methods for the purification of the product[9] from the fermentation vats are undoubtedly complicated as works processes and of limited efficiency, and giving consideration to this along with the known instability of acetaldehyde, which is also a product of the fermentation, it may be reasonably questioned as to whether it is possible to obtain what is understood as technical glycerin by this process in the amounts stated.

General Chemistry.

Probably no condition which depreciates the value of edible fats has been the subject of more frequent controversy than rancidity, and it cannot be said that we have yet a full understanding either as to the cause of rancidity or the products of the chemical reactions which bring it about. R. H. Kerr,[10] as a result of experiment and experience as well as a consideration of the theoretical possibilities involved, defines rancidity as the spontaneous oxidation of the unsaturated glycerides of fats, thus modifying the opinion of Lewkowitsch,[11] who attributed rancidity to the oxidation of free fatty acids. The development of rancidity can be absolutely prevented by the exclusion of oxygen, but with oxygen present the production of the rancid state is assisted and accelerated by such factors as light, heat, moisture, and the presence of certain metals, particularly copper and zinc. Certain bleaching earths have also

[6] J. C. Drummond, K. H. Coward, and A. F. Watson, *Biochem. J.*, 1921, **15**, 540; *J.*, 1921, 746A.

[7] *J. Biol. Chem.*, 1921, **47**, 89; *J.*, 1921, 599A.

[8] E.P. 138,328; *J.*, 1921, 57A.

[9] *Seifens. Zeit.*, 1921, **48**, 591, 677.

[10] *Cotton Oil Press*, July, 1921, p. 45.

[11] Lewkowitsch, "Chem. Tech. and Anal. of Oils, Fats and Waxes," 1913, vol. 1, p. 51

been found to have marked oxidising properties and are capable of bringing about a condition of incipient rancidity. W. N. Stokoe[12] points out that whereas micro-organisms can have no part in the production of rancidity in pure fats, since, if introduced into such fats they quickly die, in butter and margarine an adequate nidus for the development of the organisms is provided and rancid conditions quickly follow upon their growth, which is little restrained by such preservatives as are usually found, or allowed, in fatty foodstuffs, *i.e.*, salt and boron compounds. It is vitally necessary to prevent the contamination and invasion of butter and margarine by undesirable organisms which are introduced chiefly from the raw materials used in their manufacture. The resistance of mould spores to high temperature is recognised, but it would not be anticipated that deodorised oils which have been heated to a temperature as high as 150°–170° C. for several hours can contain fertile spores. Wooden barrels are considered to be unsatisfactory containers for such oils as they cannot be fully sterilised and moulds grow upon them readily.

It cannot be said that the work published during the year on the preparation of fatty acids from hydrocarbons has thrown any further light on this difficult problem. It is clear that some of the workers have realised that the highly complicated liquid oils are much less satisfactory raw materials for their oxidation processes than the simpler though still complex paraffin wax.

C. Gränacher[13] oxidised the wax by a current of air containing 2% of nitrogen peroxide. The products obtained after several days' treatment at temperatures which were varied between 110° and 150° C. consisted of a mixture of acetic, butyric, and higher fatty acids. When pure *n*-undecane was treated with nitrogen peroxide for 10 hours at 140° C., 40% of the hydrocarbon escaped oxidation and no acid of higher molecular weight than nonoic acid was found amongst the products of oxidation. This result only confirms the opinion that oxidation processes of this kind tend to a continuous reduction of the molecular weight of the oxidation products, the reduction being in great measure directly proportional to the amount of oxidation effected.

A. Schmidt[14] oxidises paraffin wax by blowing air through it for about 50 hours at 100°–120° C., and claims that the presence of a catalyst such as mercuric oxide or previously treated wax increases the rapidity of the reaction. It is necessary to separate the mixture of acids, aldehydes, alcohols, etc. from unchanged wax by distillation. F. Fischer and W. Schneider[15] have continued their work

[12] *J.*, 1921, 75T.

[13] *Helv. Chim. Acta*, 1920, **3**, 721 ; *J.*, 1921, 4A.

[14] E.P. 142,507 ; *J.*, 1921, 72A.

[15] *Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 35, 48, 101 ; *J.*, 1921, 290A.

on the oxidation of paraffin wax by treatment with air in presence of an alkali and various catalytic substances, amongst which iron, manganese, copper, cerium, titanium, fuller's earth, and charcoal are enumerated. Schmidt's claim that mercuric oxide acts as a catalyst is disputed. Various acids conforming to the general formula $C_nH_{2n}O_2$ and containing 19, 17, 15, and 13 carbon atoms have been identified in the oxidation mixture. The actual percentage of these acids of high molecular weight is not stated.

W. Schrauth and P. Friesenhahn,[16] following the old principle of alkaline oxidation originated by Schaal[17] and adopted by Fischer and his co-workers, claim that a higher percentage of fatty acids is obtained if sodium hydroxide is used as the alkali, stating that if sodium carbonate is employed anhydrides, lactones, and waxy substances are produced. It is proposed to prepare a soap from 950 kg. of a mixture in nearly equal proportions of beeswax, paraffin, and ceresin, using only 30 kg. of sodium hydroxide. Soap so produced could have little of the composition and few of the properties ordinarily associated with the material. The numerous patents which have been taken out in Germany covering the production of substances of a like kind to this which possess in small degree only the properties of soaps, lead one to the conclusion that only because of most urgent need would they have been thought of at all. "It is clear from even a cursory examination of the available literature on the subject . . . that a great deal of fundamental knowledge is lacking and that comprehensive researches must be initiated if success is to be attained. Until the complicated mixtures of hydrocarbons of many different series which exist in the natural petroleums have been studied in great and almost wearisome detail, that is until we know what we are working upon, and can separate different compounds which react specifically, we shall not solve the problem of the production of fatty acids, unless we do so by chance." [18]

Whilst the hydrolysis of fatty glycerides by means of the Twitchell reagent offers possible technical and economic advantages over the other ordinarily used methods, the process has all along suffered from the fact that the fatty acids obtained are seriously depreciated in colour and the time required to obtain a high percentage of hydrolysis is so long. The purified form of the Twitchell reagent known as "Kontakt" splitter has effected some improvement on the process, but the defects are still obvious. E. Hoyer[19] attributes this discoloration to the sulphuric acid which is used in the splitting operation, the acid being added both in the free state and combined

[16] *Chem.-Zeit.*, 1921, **45**, 177; *J.*, 1921, 226A.

[17] *J.*, 1885, 679.

[18] *J.*, 1921, 64R.

[19] *Z. Deut. Oel- u. Fett-Ind.*, 1921, **41**, 113; *J.*, 1921, 354A.

in the reagent. This statement might be accepted without question if the darkening of the fatty acids ceased with the removal of the sulphuric acid when the splitting operation is completed. It is well known, however, that Twitchell fatty acids become further discoloured on being kept for some time even after the mineral acid has been carefully removed. The Twitchell reagent is prepared by sulphonating a mixture of naphthalene and oleic acid, and it is now claimed by R. H. McKee and L. J. Lewis[20] that if the naphthalene be replaced by cymene a reagent is obtained which is cheaper, more rapid in its action, and more constant in composition than the older products. As cymene is a by-product of the manufacture of spruce wood-pulp, is easily prepared at a price at least as low as that of benzene, and is available in large quantities, the further development of its application in the manufacture of a fat-splitting reagent will be watched with much interest.

Drying Oils.

There is little doubt that our ignorance of the reactions which take place during the drying of oils is in great measure due to the fact that the preparation in the pure state of the constituents of oils, and especially those of them which are liquid at ordinary temperatures, is surrounded with so much difficulty. Until this has been done and the properties of the pure substances are known it is certain that a considerable element of doubt will surround the theories put forward to explain the varied changes which take place when oils are subjected to ordinary methods of technical preparation or use. The work of S. Coffey[21] on the oxidation of linolic and linolenic acids has evidently been prompted by a realisation of this fact. The method suggested by Erdmann[22] for the preparation of pure α-linolenic acid by fractional crystallisation from alcohol of the zinc salts of the liquid fatty acids from linseed oil has always looked to be of doubtful utility, and Coffey's careful examination of it has fully proved it to be unsatisfactory. In the course of this work Coffey obtained a mixture containing about 10% of linolenic and 90% of linolic acid, which on complete oxidation absorbed 27·1% of oxygen, and during oxidation very little acidic volatile products were formed, showing that in the drying of linseed oil the acidic substances which are produced originate wholly from the linolenic acid. By taking advantage of the method of Erdmann and Bedford[23] for producing the pure β-acid from a mixture of the α- and β-linolenic acids and deter-

[20] *Chem. and Met. Eng.*, 1921, **24**, 969; *J.*, 1921, 477A.

[21] *Chem. Soc. Trans.*, 1921, **119**, 1152; 1306; 1408; *J.*, 1921, 630A, 707A, 780A.

[22] *Z. physiol. Chem.*, 1911, **74**, 179.

[23] *Ber.*, 1909, **42**, 1324.

mining the oxidation values of the mixture and the separated β-acid, it was possible to deduce the results of the oxidation of α-linolenic acid, the form in which this acid occurs in linseed oil. The general outcome of the above work is to confirm the composition of linseed oil as given by J. N. Friend.[24] Coffey[25] has improved the method of determining the true oxygen absorption of drying oils suggested by J. N. Friend by exposing known weights of the oil distributed on filter paper to the action of oxygen in a closed vessel in presence of absorbents for the volatile products of oxidation, the apparatus being so constructed that it could be kept in a thermostat at 100° C. At this temperature it was possible to complete the oxidation of the oil in six to seven hours, whereas at ordinary temperatures absorption is not complete even after seventy days' exposure.

Our knowledge of the behaviour of linseed oil when subjected to heat has been carried forward by the work of P. Slansky[26] and of S. Coffey.[27] The former considers that the coagulation of oxidised glycerides plays an important part in the drying process, being apparently a two-stage process in which the glycerides are first oxidised and subsequently change from the sol to the gel form as is shown by the coagulation of the oil. During the period of this physical change the chemical properties of the oil are only slightly altered. He further asserts that the polymerisation of the oil on heating in absence of air proceeds similarly to the oxidation by air, solidification and the formation of an insoluble fraction taking place in an interval during which the iodine value changes by only a fraction of a unit. Coffey's experiments were carried out in absence of air under the pressure arising from heating the oil in sealed tubes to a temperature maintained between 250° and 260° C. The heated oil rapidly became lighter in colour than the original and developed the characteristic light green fluorescence of "litho oils." Examination of the heated oil at seven-hour intervals clearly exhibits the fact that after 21 hours' heating a marked thickening of the oil takes place, a change which is coincident with similar, though less distinct, breaks in the specific gravity and acid value curves. Change in the solubility of the oil in acetone was also noted during these changes. After 21 hours only 5% of the oil had become insoluble in acetone, but a further 7 hours' heating had raised this to about 25%, and after 42 hours the oil was practically immiscible with the solvent. As the hexabromide value, originally 43%, had become zero after only 7 hours' heating it is clear that polymerisation of the most highly unsaturated

[24] "Chemistry of Linseed Oil," 1917, p. 56.

[25] *Chem. Soc. Trans.*, 1921, **119**, 1152; *J.*, 1921, 630A.

[26] *Z. angew. Chem.*, 1921, **34**, 86; *J.*, 1921, 817A.

[27] *J.*, 1921, 19T.

glycerides is an early result of the heating. As the evidences of *coagulation do* not appear for some time after this, it is also certain that the products first formed undergo still further change until substances are at last formed which coagulate quickly.

A. P. West and Z. Montes[28] state that a sample of lumbang oil prepared by pressing the seeds of *Aleurites moluccana* had the following composition:—linolenin 6·5%, linolin 33·4%, olein 56·9%, glycerides of solid acids 2·8%. The oil had excellent drying properties.

Semi-Drying and Non-Drying Oils.

It is not uncommon to find references in technical and scientific literature to attempts which are being made by cultivation and selection to improve the oil content of oil-bearing seeds and nuts. That much can be done in this direction there can be no doubt, since it is well known that the composition of the constituents of the various parts of plants is strongly influenced by climate, soil, season, fertiliser, and variety. Such a process of selection as is indicated may, however, be limited in its applicability for somewhat unexpected reasons. A case in point is exhibited by recent endeavours to establish high oil-producing strains of cotton, about which it is reported[29] that "within a variety, different plants of cotton yield seed containing varying percentages of oil. High and low oil strains have been developed, but it has been found that high oil strains give a low turnout of lint. In the strains thus far established the increase of value due to the higher oil has not been sufficient to offset the low yield of fibre and they are not considered of commercial value."

The average oil content of cottonseed grown in the United States[30] during the three seasons, 1916–17 to 1918–19, was 306 lb. per ton of seed and the average meat content for the same period was 978 lb. per ton of seed. The seed produced in Mississippi, North Carolina, and South Carolina yielded more than 320 lb. of oil per ton, whilst that produced in Louisiana, Mississippi, and Oklahoma produced more than 1000 lb. of meats per ton. That variety has a considerable effect upon the composition of the oil obtained from seeds is made evident also by the results of the examination by G. S. Jamieson, W. F. Baughman, and D. H. Brauns[31] of two samples of arachis oil prepared respectively from Spanish type and Virginia type nuts:—Unsaponifiable matter, 0·2, 0·3%; olein, 52·9, 60·6%; linolin, 24·7, 21·6%; palmitin, 8·2, 6·3%; stearin, 6·2, 4·9%; arachidin, 4·0, 3·3%; and ligno-

[28] *Philippine J. Sci.*, 1921, **18**, 619; *J.*, 1921, 896A.
[29] *Ann. Rept., Texas Agric. Exp. Station,* 1920.
[30] *U.S. Dept. Agric., Bull.* 948, Aug., 1921.
[31] *J. Amer. Chem. Soc.*, 1921, **43**, 1372; *J.*, 1921, 740A.

cerin, 3·1, 2·6%. In neither case could hypogæic acid be detected. Besides the internal variations of these figures, they differ in several respects from those hitherto published for this oil.

The published chemical characteristics of kapok oil are so variable that the results of a recent examination of Indian kapok seed[32] obtained from *Bombax malabaricum* are of undoubted interest. The seeds, which contained 8·9% of moisture, yielded 22·3% of a bright yellow oil which had the following characteristics :—Sp. gr. 0·9208 at 15° C. ; acid value, 9·3 ; saponif. value, 193·3 ; unsaponifiable, 1·0% ; $n_D^{40}=1·461$; titre, 38·0° C. The low iodine value of this oil compared with that of the oil obtained from the seeds of *Eriodendron anfractuosum*, which are shipped to Europe as Java kapok seed, explains the many seeming discrepancies in the published analyses of the oil, especially since the latter seed appears in much larger quantities in the market. An interesting examination of certain seeds sold as mustard seed is reported by A. Viehoever, J. F. Clevenger, and C. O. Ewing.[33] They were found to be Chinese colza, *Brassica campestris chinoleifera*, Viehoever, n. var. The volatile oil from the seeds proved to be crotonyl isothiocyanate, a known constituent of rape seeds which cannot replace mustard oil in its ordinary applications. The fatty oil had all the general characteristics of rape oil.

Oil from the seeds of the cantaloup melon. *Cucumis melo* L., has been examined by W. F. Baughman, D. Brauns, and G. S. Jamieson,[34] who state that it consists of glycerides of myristic acid 0·3%, of palmitic acid 10·2%, of stearic acid 4·5%, of oleic acid 27·2%, and of linolic acid 56·6%; unsaponifiable matter 1·1%. In spite of the presence of so high a percentage of the glycerides of linolic acid no film developed even after a week's exposure to air on a glass plate.

The possibility of using lemon seeds, which are obtained in large quantities in various branches of the citrus industry, as a source of oil is again raised by the publication by Bertolo[35] of the results of his examination of the so-called *pastazzo*. From 30 to 35% of oil can be obtained from this material by extraction with solvents, and this would appear to be the only satisfactory means of obtaining it, as the peculiar character of the material precludes the use of a pressure process. It has a dark yellow colour and retains a pronounced odour of lemons even after being washed with hot water or dilute sulphuric acid. Considerable quantities of orange and lemon seeds are obtained in this country as a by-product of fruit-preserving operations, and it might be possible to use them as a

[32] *Bull. Imp. Inst.*, 1920, **18**, 335 ; *J.*, 1921, 396A.
[33] *J. Agric. Res.*, 1920, **20**, 117 ; *J.*, 1921, 89A.
[34] *J. Amer. Chem. Soc.*, 1920, **42**, 2398 ; *J.*, 1921, 89A.
[35] *Giorn. Chim. Ind. Applic.*, 1920, **1**, 48 ; *J.*, 1921, 153A.

source of oil and preferably if they can be worked in a reasonably fresh state. The oil obtained by Bertolo contained only 2·82% of free fatty acids, whereas oil extracted by the writer from lemon seeds accumulated at a works in this country and which had been kept in a heap for some time contained over 30% of free fatty acids. The chemical characters of the oil, which is of semi-drying type, are already well known.

E. André[36] has examined eleven samples of grape-seed oil obtained from different sources and confirms previous observations as to the great irregularity in its physical and chemical characters.

The comparatively high acetyl value of some samples of the oil (45–50) is especially noteworthy. It is suggested by B. Rewald[37] that technical use might be made of the large quantity of the seeds of the "donkey thistle" (*Cynara cardunculus*) which is obtainable in the Argentine. They contain 41–44% of an oil which has the following characters :—Sp. gr. at 15° C., 0·9242 ; solidif. pt., 13° C. ; $n_D^{15}=1·4770$; acid value, 1·63 ; iodine value, 119. The pressed cake contains : moisture, 0·52 ; ash, 4·43 ; oil, 10·96 ; proteins, 52·5 ; crude fibre, 17·99%. E. H. Ducloux[38] who has also examined the oil generally confirms Rewald's figures and states that the oil in many respects resembles cottonseed oil.

Solid Fats.

A. Heiduschka and A. Steindruck,[39] who have examined the product obtained from the mixed fatty tissues of the horse, found it to have m.p. 32·3° C., sp. gr. 0·9224 at 15° C., $n_D^{40}=1·4617$, acid value 2·62, saponif. value 203·9, Reichert-Meissl value 0·42, Polenske value 0·37, iodine value 75·17, acetyl value, 14·12. The mixed fatty acids were found to consist of linolenic acid, 1·7% ; linolic acid, 6·7% ; oleic acid, 55·2% ; stearic acid, 6·8% ; palmitic acid, 29·5%. The acids also contained 0·43% of unsaponifiable matter mainly cholesterol.

Mixed glycerides have been identified in the solid constituents of goose fat by C. Amberger and K. Bromig.[40] About 15% of stearin, which had iodine value 52·3, was separated and was found to contain α-stearodipalmitin, m.p. 57·4° C., and β-stearodipalmitin, m.p. 63·0° C. The liquid portion of the fat, which had iodine value 77·0, consisted mainly of triolein. Oleodipalmitin, m.p. 33·5° C., was identified in both the solid and liquid portions of the fat. Otoba butter, obtained from the seeds of *Myristica otoba*, which is of frequent occurrence in tropical America, has been found

36 *Comptes rend.*, 1921, **172**, 1296, 1413 ; *J.*, 1921, 477A, 518A.
37 *Chem.-Zeit.*, 1921, **45**, 805 ; *J.*, 1921, 707A.
38 *Anal. Soc. Quim. Argentina*, 1920, **8**, 410 ; *J.*, 1921, 396A.
39 *J. prakt. Chem.*, 1921, **102**, 241 ; *J.*, 1921, 665A.
40 *Pharm. Zentralh.*, 1921, **62**, 547 ; *J.*, 1921, 740A.

by W. F. Baughman, G. S. Jamieson, and D. H. Brauns[41] to consist of the glycerides of myristic and, to a lesser extent, lauric acids. Traces of palmitic and oleic acids were also present. Besides otobite, found by Uricoechea in the unsaponifiable matter, another compound named by the authors iso-otobite, has also been identified.

Marine Animal Oils.

C. Grimme[42] gives the composition of a sample of herring oil fatty acids as:—saturated acids, 20%; oleic acid, 20%; linolic acid, 33%; linolenic acid, 17%; clupanodonic acid, 9%. The separation of the various unsaturated acids was arrived at by taking advantage of the varying solubility of their bromine compounds in various pure and mixed solvents. The existence of the highly unsaturated acid having the formula $C_{22}H_{34}O_2$, mentioned by Tsujimoto[43] as occurring in Japanese sardine oil, is considered by the author not to be proved. T. Lexow,[44] however, mentions this acid, as also another highly unsaturated acid having the formula $C_{20}H_{30}O_2$, as being amongst the proved constituents of the oil. A possible explanation of Grimme's failure to detect these acids in herring oil may be found in the fact noted by Lexow that the iodine value of herring oil, as also the yield of oil from the fish, varies markedly with the season of the year. In July, August, and September a yield of 13% of oil having an average iodine value of 149 is obtained, whilst in March the yield is only 2% and the average iodine value 110. It has also been noted that whilst the saponification value is practically unaffected by the season of the year, this value, as also the percentage of unsaponifiable matter, varies considerably with the latitude in which the fish is caught.

The liver oil from the sea-wolf (*Anarrhichas lupus*, L.) is stated by T. Lexow[45] to be characterised by its low iodine value and high percentage of unsaponifiable matter. Oils from the livers of both male and female fish were examined with the following results:—yield on the weight of liver 29·6% and 34·5% respectively. The oils had iodine values, 131·2 and 118·1, and contained unsaponifiable matter equal to 5·23 and 3·86%.

Waxes.

Montan wax, which is obtained from lignites by extraction with solvents, still gives rise to a considerable amount of interest on the Continent. Since lignite, as mined, always contains a considerable proportion of moisture, and drying is costly, satisfactory

[41] *J. Amer. Chem. Soc.*, 1921, **43**, 199; *J.*, 1921, 267A.
[42] *Chem. Umschau*, 1921, **28**, 17; *J.*, 1921, 267A.
[43] *J. Chem. Ind. Tokyo*, 1920, **23**, 1007; *J.*, 1920, 825A.
[44] *Chem. Umschau*, 1921, **28**, 85, 110; *J.*, 1921, 438A.
[45] *Chem. Umschau*, 1921, **28**, 213; *J.*, 1921, 779A.

extraction is best obtained by using such a solvent as a mixture of alcohol and benzol[46] in which a considerable amount of water can be held without depreciating the solvent capacity for the wax. It is now suggested by E. Donath[47] that acetone is to be preferred to this mixture, since it is a common solvent for both wax and water and is quite as efficient as benzol when applied to Bohemian lignites.

Attempts to obtain montan wax from several low-temperature tars derived from lignite have shown that although the wax can be identified in some quantity in the tars, the yield obtained by superheated steam distillation is so low that decomposition of the wax clearly takes place. The wax is now being applied to the sizing of paper, patents covering its application for this purpose being held by J. W. Zanders[48] and H. T. Böhme A.-G.[49]

Mutton-bird oil, which is extracted from the stomach of *Aestrelata lessoni*, a petrel peculiar to Australia, has been examined by C. L. Carter.[50] The oil, which in many ways resembles sperm oil and must be regarded as a liquid wax, was of light straw colour, and had a faint and not unpleasant odour. It had the following characteristics :—Sp. gr. at 15·5° C., 0·884 ; free fatty acids, 2·23% ; higher alcohols, 38·4% ; saponif. value, 119·6 ; iodine value, 130 (Wijs). The mixed alcohols, which had m.p. 31°–31·5° C., were found to consist chiefly of cetyl alcohol, whilst the mixed fatty acids obtained after saponification consisted in the main of oleic acid though their high iodine value indicates the presence of a certain proportion of acids of the linolic or linolenic series.

Hardened Fats.

The importance of the process of hydrogenation applied to fats has undoubtedly been lessened by the continuous appreciation in the proportionate value of the formerly cheap liquid oils to which the process was generally applied, and there is no doubt that the very general adoption of the process has itself been the cause of the increase in value which is now acting as a deterrent to the continued extension of its application. Improvements in the process most generally show themselves now in modifications of the catalyst, generally with the result of increasing its activity and extending its life. The effect of the association of some compound of alumina with the nickel in bringing this about is made evident by several patents. E. Sittig and A. Granichstädten[51]

[46] G.P. 325,165 ; *J.*, 1920, 814A.
[47] *Brennstoff-Chem.*, 1920, **1**, 86 ; 1921, **2**, 28 ; *J.*, 1921, 138A.
[48] G.P. 303,342 ; *J.*, 1921, 384A.
[49] G.P. 331,472 ; *J.*, 1921, 384A.
[50] *J.*, 1921, 220T.
[51] E.P. 147,578 ; *J.*, 1921, 857A.

have protected the use of a catalyst prepared by the reduction in hydrogen of the gelatinous precipitate obtained when a soluble nickel salt associated in solution with a salt of magnesium or aluminium is precipitated with silicate of soda. It is claimed that this catalyst possesses special deodorising properties. Similarly, De Nordiske Fabriker De-no-fa Aktieselskap[52] have patented the precipitation and reduction of nickel aluminate, sodium aluminate being employed in this case as the precipitant. As a preventive of the poisoning of the catalyst by the formation of metallic soap resulting from the action of free fatty acid on the catalyst, E. R. Bolton and E. J. Lush[53] add a small quantity of mono- or diglycerides of fatty acids to the oil to be hydrogenated. This combines with any free fatty acid present or formed during hydrogenation and so prevents attack on the nickel. E. F. Armstrong and T. P. Hilditch[54] have continued their investigation of the hydrogenation process, studying in particular surface area in relation to activity as well as the effect upon the rate and extent of reaction, of the specific nature of the catalyst. Having correlated the apparent volume of various catalysts with their activity, they especially point out the high apparent volume of nickel hydroxide reduced on kieselguhr compared with an unmounted catalyst. They further ascribe the variations in the catalytic power of reduced nickel to the different surface areas, which variations do not require for their interpretation the assumption of the presence of any catalyst (such as oxide) other than metallic nickel.

[52] E.P. 140,371 ; *J.*, 1921, 90A.
[53] E.P. 162,382 ; *J.*, 1921, 438A.
[54] *Proc. Roy. Soc.*, 1921, **A99**, 490 ; *J.*, 1921, 707A.

PAINTS, PIGMENTS, VARNISHES, AND RESINS.

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There has been a growing tendency of late years for writers of specifications to demand only that certain physical properties shall be shown by the specified material, the question of composition and the problem of how to get the desired properties being left to the manufacturer. No doubt one of the determining factors which led to this method of specifying by properties was the inability of the analyst to determine the chemical composition of the required product, but also it has gradually become recognised that, in the majority of cases relating to the group of materials now under review, very little is known as to the relation between the so-called "chemical composition" and physical properties; it is remarkable, however, how much faith is still placed on the results of a chemical analysis. The specifying of physical properties necessitates a knowledge of how to test these properties, and consequently this change of attitude on the part of specification writers has been reflected in the literature by the appearance of fewer papers on chemical analysis and by a marked increase in the number of published investigations dealing with the physical properties of varnishes, paints, and pigments. The application of the results of these investigations to the needs of a specification is of minor importance compared with the valuable information which they afford regarding the constitution of the various products and the changes that take place in the components during manufacture and during the drying and weathering of varnish and paint films. Furthermore the method of specifying by properties stimulates research, invention, and progress on the part of the manufacturer. It is to be feared, however, that, since research has not yet been collectively organised by the manufacturers concerned in this group of industries, the rate of progress in Great Britain is slower than it ought to be. The regrettable fact has to be recorded that the proposal to form a research association in this country received only moderate support at the hands of the National Federation of Paint, Colour and Varnish Manufacturers. The cry is for fundamental research

rather than for investigations which will attack problems directly by methods based on past experience without seeking to investigate the fundamental nature of the process.[1]

PAINTS AND PIGMENTS.

It has long been universally recognised that both the durability and the "finish" of a dried paint film are dependent to a considerable extent upon "fineness of grinding." Moreover, it is understood in a general sort of way that the latter term involves not only the fineness of division of the pigment when in the dry condition, but also the extent to which the pigmentary particles have been dispersed throughout the medium. The full importance of the degree of dispersion in this connexion does not, however, seem to have been sufficiently realised. There is a large field for investigation as to how this degree of dispersion depends upon the size of pigmentary particles, the specific natures of both pigment and medium, and upon the mode and extent of grinding pigment and medium together. H. L. Sulman[2] has shown, in connexion with ore flotation, that the degree of dispersion of a two-phase system, the continuous phase of which is water, is dependent upon the degree of wetting of the disperse phase by the continuous phase, and R. P. L. Britton[3] in a suggestive paper dealing with the physical chemistry of paint and varnish, points out that the ease with which a pigment can be wetted, or saturated, with the medium in which it is ground is an important factor in determining the fineness of grinding produced in enamels. Britton goes so far as to state that the term "fineness of grinding" is in many cases a misnomer, the thickness of an ordinary film of varnish being eight or ten times the diameter of the largest particles of zinc oxide, and that the principal action during the grinding of pigment and medium together is to force the liquid into the solid particles to the point of saturation of the latter. The exact meaning to be attached to this last statement is not quite clear, and since the suggestion is one which in the present state of our knowledge concerning the physics of solid particles is rather difficult of conception, it would seem preferable at present to consider the matter from the point of view of dispersion and deflocculation, although when the work of I. Langmuir[4] has been further developed, Britton's point of view may prove the more fruitful. This subject has also attracted the attention during the past year of H. A. Gardner and R. E. Coleman.[5] These authors distinguish between the terms "texture" and

[1] See *Report of Committee for Scientific and Industrial Research*, 1920–21.

[2] *Bull. Inst. Min. and Met.*, No. 182, Nov., 1919; *J.*, 1920, 27A.

[3] *J. Oil and Colour Chem. Assoc.*, 1920, **3**, 138.

[4] See *e.g. Trans. Faraday Soc.*, 1920, **15**, 62.

[5] *Circ.* 117, *Paint Manufacturers' Assoc. U.S.*; *J.*, 1921, 227A.

"fineness" as applied to pigments. Whereas the terms "coarse" and "fine" refer to the extent of the subdivision of the particles constituting a mass, the term "texture" is defined as the property of pigments to disperse readily and become finely divided when mixed with a liquid. Pigments are said to be of "soft texture" if they disperse readily when lightly ground in a mixture of blown linseed oil and turpentine. Certain liquids will, however, cause flocculation in pigments, and thus a particular pigment may show a "soft texture" towards one medium and yet be of "hard texture" when mixed with another medium. Although this definition of texture is somewhat arbitrary, it describes a property of pigments which well repays examination in a pigment-testing laboratory, and is a step in the right direction of reducing to first principles the confusion that undoubtedly exists among paint manufacturers with regard to the use of the expression "fineness of grinding." It seems doubtful, however, whether the use of the terms "texture," "hard," and "soft" in this connexion sufficiently emphasises the rôle of the medium.

In a review of the methods available for determining the size of particles C. A. Klein and W. Hulme [6] draw attention to the importance of knowledge as to the size of pigmentary particles and to the fact that the amount of published data on the subject is deplorably small. After adversely criticising the use of a screen, and also the method of subsidence in a liquid, these authors describe a modification of Schöne's [7] elutriator as used by them. The various fractions consisting of approximately equi-sized particles have been examined microscopically, and the results expressed in a graphic method in which various sized particles are represented by different coloured areas, the extent of such area being proportional to the weight and particular size. Interesting results have already been obtained by the application of this method of mechanical analysis to the question of dry-grinding of barytes, showing how the degree of fineness varies with the time of grinding and with the type of mill used. Further results are promised by these authors on this and other cognate subjects, such as the relationship between size of particles and the important factors known as bulking value, oil absorption, and re-inforcement of paint films. These results will be awaited with considerable interest. With regard to the use of screens, which undoubtedly have a certain value in the approximate grading of powders, the experience of Klein and Hulme is to the effect that screens finer than 200-mesh are not satisfactory. C. D. Holley, [8] however, states that, as the result of eight years' experience with the so-called 350-mesh screen which he developed and intro-

[6] *J. Oil and Colour Chem. Assoc.*, 1920, **3**, 177.

[7] *Z. anal. Chem.*, 1868, **7**, 29.

[8] *Paint, Oil, and Chemical Review*, No. 21, Vol. 72, Nov. 23, 1921.

duced to the paint trade in 1915, the use of such a screen has been found eminently useful and practical in all respects. These screens were originally made in France, but have not been manufactured there since the war. They are now being made in America, however, with wire having a diameter of 0·0014 inch, the apertures being 0·0017 inch in diameter. Holley cites an instance where the cost of grinding a high-grade white paint was reduced approximately 50% by using white lead having a residue of 0·5% on the screen instead of white lead having a 2·5% residue.

Not infrequently the term "fineness of grinding," when applied to paint or enamel, involves further the question of "consistency" or fluidity—that property which governs the smoothing-out qualities of the paint so that the dry film is free from brush marks, humps, depressions, etc. In any case, "consistency" and "grinding" are intimately connected, and, whilst the existence of this relationship has always been recognised more or less vaguely by manufacturers, the sorting out of the scientific principles underlying it only became possible after the epoch-making investigations of E. C. Bingham[9] on plasticity and the point of zero fluidity. His work demonstrated the fact that the measurements "yield value" and "mobility" completely express the plastic nature of a substance. Later, E. C. Bingham and H. Green[10] extended these ideas to paints and showed that paint is plastic, its "consistency" depending both upon its yield value and its mobility. H. Green[11] has now described further improvements and developments of the plastometer and its practical application to research and routine problems in the paint industry. This author[12] has clearly shown that the consistency of a paint is dependent upon the degree of dispersion of the pigment, which in turn involves the degree of wetting of the pigment and its particle size. Bearing upon this question, a valuable suggestion has been made by W. D. Bancroft[13] with reference to the amount of oil which should be used for the grinding of pigment pastes. He states that the amount of oil now used for a given pigment is very arbitrary, and the values given by experts often differ widely. The suggestion is made that reproducible figures could be obtained if in each case there was determined the amount of oil necessary to give zero fluidity, and, since this is more oil than manufacturers wish to use, some definite fraction of this amount might be adopted as the standard. The relation between consistency and size of particles is further emphasized by F. P. Ingalls,[14] who states that it makes

[9] *U.S. Bureau of Standards, Sci. Paper No.* 278, 1916.

[10] *Proc. Amer. Soc. Testing Mat.*, 1919, **19**, 640; *J.*, 1920, 495A.

[11] *Ibid.*, 1920, **20**, Part 2, 451.

[12] *Ibid.*, 1921.

[13] *J. Ind. Eng. Chem.*, 1921, **13**, 157.

[14] *Circ.* 135, *Paint Manufrs. Assoc. U.S.*

a great deal of difference whether there is a wide range between the maximum and minimum size or whether the particles are more nearly uniform. As the particles become finer the tendency to flocculation increases, and, unless counteracted by the dispersive power of the vehicle, all sorts of changes in the consistency and applicability of the paint may ensue. This has an important bearing upon the choice of a correct medium to suit a particular pigment, or, considered from the opposite point of view, upon the proper blending of pigments to suit a particular medium. F. G. Breyer[15] states that most livering, thickening, or thinning down of paints on standing can be explained on the grounds of continuous increased or decreased wetting of the pigment by the vehicle. Attention has been drawn to the same point by R. P. L. Britton.[3]

Writing on recent developments in spray painting, H. A. Gardner[16] emphasises various advantages obtained by the use of the spray gun, and gives the results of some exposure tests on the relative durability of spray *versus* brush painting. Attention is also drawn to various points in connexion with the drying and flowing properties of spray paints, and to the importance of obtaining the correct thickness of film. In this connexion attention is drawn to the "film gauge" recently devised by A. H. Pfund for measuring the thickness of wet paint films. In his original paper Pfund[17] gives a number of measurements for the thickness of paint films brushed out on glass which agree, to within 3%, with those calculated from weight of paint and area of surface. Also spreading rates of three different paints were measured when brushed on primed wood by four different painters. The results varied enormously—nearly 100% in one case—and showed that greater differences, as regards spreading rates, exist between individual painters than between different paints. As a result of several hundred tests upon a large number of paints applied to different kinds of surfaces, H. A. Gardner and P. C. Holdt[18] conclude that the instrument is accurate to within 25%. In the present writer's opinion the chief use for the apparatus would be in the paint research laboratory.

As regards the durability of paint films as judged by carefully carried out exposure tests, several results have been recorded during the past year. The main point which emerges from the results of J. A. N. Friend[19] is the marked superiority of litho oil as a medium over raw or "boiled" linseed oil. This is attributed in part to diminished permeability towards water, but mainly to the greater "stability" of the litho oil owing to the saturation of the double

15 *Circ.* 135, *Paint Manufrs. Assoc. U.S.*
16 *Circ.* 114, *Paint Manufrs. Assoc. U.S.*
17 *J. Franklin Inst.*, 1921, **191**, 517; *J.*, 1921, 356A.
18 *Circ.* 132, *Paint Manufrs. Assoc. U.S.*
19 *J. Iron and Steel Inst.*, 1921, **103**, 365; *J.*, 1921, 393A.

bonds (which takes place during polymerisation) rendering the oil less liable to oxidation and disintegration on exposure. Amongst the conclusions reached by H. A. Gardner[20] is the fact that, in aluminium paints, there is no advantage in using polished aluminium powder over the unpolished, also that 300-mesh powder has no superiority over the 200-mesh material. A critical survey as to the methods of carrying out exposure tests and the value to be placed on the results obtained thereby is made by C. A. Klein.[21] The question as to the best pigments to be used in paints designed for the protection of metal surfaces is one on which there is, at present, fair agreement amongst paint technologists, and there has been little published on this matter during the last few years. There are still some fallacious ideas prevalent, however—chiefly in connexion with the use of graphite and black paints—and attention should therefore be drawn to an admirable summary by H. A. Gardner[22] of substances used in such paints. A recent paper by J. A. N. Friend[23] on a colloid theory of the corrosion of iron should also be consulted by those who are interested in the question of the protection of iron. Remarkable results have been obtained showing the effect of moving water on the corrosion of iron immersed in it. The influence of dissolved electrolytes, protective colloids, alkalis, and other substances has also been studied.

Owing to the action of the Governing Body of the International Labour Office, much has been written during the past year in scientific and in technical journals, as well as in the daily Press, on what has come to be called the white lead controversy. As regards the relative merits of white lead and other white pigments few, if any, new facts have been brought forward on either side. It is rather surprising, however, that during the discussion little has been heard about the comparatively new pigments containing titanium and antimony. It seems remarkable, too, that so little reference should be made to the part played by the medium in paints; it is idle to talk about the relative merits of two or more pigments unless it is stipulated that the same medium be used in each case. Another curious feature of the controversy is the total disregard of all other compounds of lead other than white lead. The chief points discussed during the past year, however, have ranged round the hygiene of the painter, the reliability of statistics, and the degree of accuracy with which cases of white lead poisoning may be diagnosed. In a lengthy but very interesting paper, H. E. Armstrong and C. A. Klein[24] describe elaborate and detailed

[20] *Circs.* 129 *and* 130, *Paint Manufrs. Assoc. U.S.*

[21] *Oil and Colour Trades J.*, 1921, **59**, 2445.

[22] *Amer. Electrochem. Soc.*, 1921.

[23] *Chem. Soc. Trans.*, 1921, **119**, 932; *J.*, 1921, 545A.

[24] *J. Roy. Soc. Arts*, 1921, **69**, 655.

experiments on the question of the splashing which occurs during the operations of a painter. These experiments show, amongst other results. that painters do not inhale splashes, that splashes readily fall to the ground, and that not even a minute spray remains suspended in the air. In the same paper the question of the toxic effect of turpentine and other volatile thinners is discussed, and some interesting curves are given showing the comparative rates of volatility of a number of thinners and also their rates of evaporation from paints. It occurs to the present writer that perhaps useful information as to the toxic effect of thinners might be obtained from statistics relating to the health of persons engaged in varnish manufacture, as distinct from paints. Owing to the judicious interposition and appeal of Dr. Legge, the representative of the British Government at the International Labour Conference in November last, an excellent compromise was arrived at, and it thus seems probable that the recent activities displayed by the controversialists will decline. It is to be hoped, however, that immediate steps will be taken towards legal enforcement of the regulations relating to the use of white lead which were recommended at Geneva.

Referring to the evaluation of white pigments, H. E. Clarke [25] attempts to clarify existing ideas as to the use of the terms spreading power, hiding power, and opacity. This author restricts the use of the term hiding power to pigments, whilst the term opacity is applied to paints. Many interesting points concerning the use of antimony oxide as a pigment are to be found in the same paper and in the lengthy discussion which followed it. The right of both antimony oxide and titanium oxide to be classified amongst the well-recognised white pigments appears to be now established. These pigments differ so much, however, in chemical character from the basic white pigments around which the prevalent ideas of paint mixing have developed, that they should, in fairness to all concerned, be used with caution by those whose knowledge of paint technology is restricted. Three patents [26] by the Titan Co. A/S, referring to improvements in the process of manufacture of titanuim white, have appeared recently. Of several patents [27] referring to the production of new lake colours the most interesting appears to be that granted to the British Dyestuffs Corporation, Ltd., J. Baddiley, and J. Hill.[28] The colour therein described is a yellowish-scarlet lake of great beauty

[25] *J. Oil and Colour Chem. Assoc.*, 1921, **4**, 2.

[26] U.S.P. 1,360,737 and 1,368,392; *J.*, 1921, 52A, 228A. E.P. 149,316; *J.*, 1921, 552A.

[27] Ultro-Chem. Corp., U.S.P. 1,358,007 and 1 369,252; *J.*, 1921, 228A, 269A.

[28] E.P. 164,053; *J.*, 1921, 504A.

of shade and resembles the colours of the Ponceau class, but is very much superior to the latter in its fastness to light. It is obtained in the usual manner from the monoazo dyestuff derived from *m*-xylidinesulphonic acid and R-salt. The introduction of certain tungstic compounds during the process of precipitation of lakes is claimed by F. Bayer und Co.[29] and by the Chemical Foundation Inc.[30] as a method of increasing the fastness to light of the lakes so produced.

In 1916 L. A. Keane[31] found that the yellow colour of bricks was due to the finely divided condition of the anhydrous ferric oxide present, and that alumina was the important peptising agent. In the following year F. H. Scheetz[32] prepared stable mixtures of yellow ferric oxide and alumina by precipitating solutions of ferrous and aluminium sulphates with calcium hydroxide, and heating the precipitate to 1000° C. J. H. Yoe[33] has now confirmed and extended this work, and has obtained stable mixtures containing 8% of Fe_2O_3 and 92% of Al_2O_3 on the one hand, and 6% of Fe_2O_3 with 94% of $BaSO_4$ on the other. These mixtures are yellow or buff in colour, and, whilst at present they may be only of passing interest, there may, quite conceivably, arise a demand for such a pigment. An interesting observation bearing upon the well-known fact that in certain paints the colour of Prussian blue is gradually destroyed, is made by F. Fritz,[34] who states that if a small quantity of Prussian blue be allowed to stand for a long time in contact with oxidised linseed oil, decolorisation of the pigment takes place if a sufficient amount of moisture is present. The latter proviso is very significant.

The problem of measurement of colour is one which is of vital interest to many industries, but in none probably is it more perplexing than in its application to pigment and paint mixing. It is very desirable that the colours of paints should be capable of being colorimetrically analysed and synthesised, so that it might be predicted with certainty that by mixing certain pigments a product of the desired colour would result. Valuable papers embodying the results of experiments bearing upon this question, and which must eventually assist in attaining the desired end, have been published by C. E. K. Mees,[35] by A. E. Bawtree,[36] and by T. M. Lowry.[37] When grading a number of white pig-

[29] E.P. 143,242; *J.*, 1921, 385A.
[30] U.S.P. 1,378,882; *J.*, 1921, 539A.
[31] *J. Phys. Chem.*, 1916, **20**, 73?; *J.*, 1917, 138.
[32] *Ibid.*, 1917, **21**, 570; *J.*, 1917, 1270.
[33] *Ibid.*, 1921, **25**, 196; *J.*, 1921, 356A.
[34] *Chem. Umschau*, 1920, **27**, 242; *J.*, 1921, 90A.
[35] *J. Ind. Eng. Chem.*, 1921, **13**, 729.
[36] *J. Oil and Colour Chem. Assoc.*, 1921, **4**, 166.
[37] *Ibid.*, 1921, **4**, 180.

ments, ranging from a yellowish tint to a bluish tint, it is very difficult to decide which is the "most correct white," and opinions will differ widely in this respect according to the taste of the observer. Scientifically, white is more difficult to define than any other colour, and its definition is more or less arbitrary. The light of the mid-day sun (blue sky light excluded) reflected from a non-selective surface is white, but the difficulty is to be certain of the non-selective character of the standard surface used. Moreover, any attempt to put the subject of the grading of white paints on a scientific basis must involve not only a method of deciding as to whether or not a surface is white, but also a method of quantitatively indicating slight departures from white. Previous attempts in this direction have been unsuccessful owing to the fact that the departure from white is so small that accurate measurements of that departure are out of the question. A. H. Pfund,[38] however, has recently devised an instrument which shows every promise of becoming a valuable, and almost indispensable, piece of apparatus to the paint technologist. In this new colorimeter for white pigments the principle of multiple reflections is adopted in order to accentuate departure from white, and a piece of ground optical glass is used as a non-selective reflecting surface. In order to obviate the necessity of standardising a source of white light, the colour characteristics of the paint are given in terms of "brightness" for colours of dominant hue 460 $\mu\mu$ (blue), 550 $\mu\mu$ (green), and 625 $\mu\mu$ (red), respectively. In this way the colour characteristics are established uniquely and standard samples of paints may be discarded. This method of investigation shows that all "white" pigments are yellowish, though when compared with one another some may be pinkish, bluish, etc. By the addition of a trace of lampblack to a zinc oxide paint, the latter becomes nearly non-selective, and whereas the "brightness" of the paint is diminished by only 3·5%, its hiding power is increased by 17·5%.

Varnishes and Drying Oils.

In order to obtain uniformity in the brushing and flowing-out qualities of a varnish it has long been the custom to apply some sort of "viscosity" test, but of recent years it has gradually become recognised that measurements on "consistency" may afford valuable information as regards the constitution and history of the varnish. The importance of viscosity in the study of the colloid state was pointed out by Wo. Ostwald[39] so long ago as 1913, or possibly earlier, but probably the first published investigation

[38] *Proc. Amer. Soc. Testing Mat.*, 1920, **20**, Part 2, 440.
[39] *Trans. Faraday Soc.*, 1913, **9**, 34.

relating to this aspect of viscosity determinations as applied to varnishes was that of M. Y. Seaton, E. J. Probeck, and G. B. Sawyer,[40] who studied viscosity-temperature changes and obtained very striking results. In view, however, of the fact that the viscosities were determined by the Doolittle instrument, and of the importance attaching to the deductions arrived at, the present writer feels that these results need confirmation. The desirability of studying the viscosity of heterogeneous systems at different rates of shear was pointed out in 1913 by E. Hatschek,[41] who showed that certain emulsoid sols possessed different viscosities at different rates of shear below certain limits, and, in 1920, A. E. Bawtree[42] emphasised the importance of determining the viscosities of varnishes under different rates of shear in order to obtain some idea as to their colloidal character. Referring to his experiments on stand oil Bawtree states that the various times of efflux under different pressures give a "clear mental picture of the colloidal structure of the fluid, while the particular value at 100 mm. pressure gives a useful comparison as to general stoutness." The various papers by E. C. Bingham and H. Green bearing on consistency have dealt chiefly with clays and paints, but during the past year H. A. Gardner and P. C. Holdt[43] have applied the Bingham plastometer to the measurement of consistency of varnish. Over fifty samples of commercial varnishes, whose absolute viscosities ranged from 0·6 to 5·5 poises at 25° C., were examined, but in only a few of these was any indication of plasticity found, and in most of these few cases the "yield value" was very small. The existence of a high yield value corresponded with stringy consistency and poor working qualities in the varnish. In the same paper descriptions of various other types of viscometers are given, and comparison has been made between the Bingham instrument, the McMichael and the Doolittle viscometers. The method described by W. H. Herschel[44] has been used for calculating absolute viscosities from readings on the McMichael instrument, but the values so obtained are in only fair agreement with corresponding values from the Bingham apparatus, whilst readings on the Doolittle viscometer appear to bear no definite numerical relation to absolute viscosities. A certain amount of evidence, mainly from the use of the McMichael instrument, is brought forward in support of the view, which has frequently been suggested before, that certain varnishes possess a structure which may be broken down by shear resulting from violent agitation or pressure.

[40] *J. Ind. Eng. Chem.*, 1917, **9**, 35; *J.*, 1917, 148.
[41] *Trans. Faraday Soc.*, 1913, **9**, 88–91.
[42] *J. Oil and Colour Chem. Assoc.*, 1920, **3**, 119.
[43] *Circ.* 127, *Paint Manufrs. Assoc. U.S.*
[44] *J. Ind. Eng. Chem.*, 1920, **12**, 282; *J.*, 1920, 430A.

The evidence, however, is not conclusive, though in view of the well-known behaviour of certain greases under similar conditions the suggestion cannot be said to be improbable. It seems curious, however, that more definite indications were not forthcoming from the results obtained with the Bingham apparatus. One of the most important applications of the latter instrument should be in the investigation of certain undesirable qualities in varnishes and of the changes that take place on ageing. That some of such changes may be due to change in surface energy relations resulting in a gradual increase in the size of particle aggregates is suggested by the present authors, and a similar view has also been put forward by *R. P. L. Britton.*[3] *The latter writer states further that* in some other cases the "sugaring up" of varnishes may be due to the reversion of superfused resins to the crystalline state. Gardner and Holdt, in the paper referred to above, give the result of an ultramicroscopic examination of varnishes. The number of particles per c.c. is given for a large range of different types of varnishes, but there is no sort of parallelism between the number of particles of the disperse phase and the type of varnish. The Brownian movement is almost completely damped by the viscosity of the varnish. The samples of high viscosity showed either a very large number of small particles or a smaller number of very large particles, the size being indicated by their relative brightness.

That many of the problems relating to the drying and weathering of varnish films can be explained only by paying more attention to surface concentrations and to changes in surface energy has been pointed out by R. S. Morrell,[45] and it would appear desirable therefore that more data should be available respecting the surface tensions and interfacial tensions of varnishes and of varnish components. No doubt such values would provide a certain amount of useful information, but on the other hand it is difficult to see how exactly in the present state of our knowledge regarding the surface energy of solids, the results could be applied to the problems in question. In his presidential address to the Oil and Colour Chemists' Association R. S. Morrell[46] gives new values for the surface tension to air and interfacial tension to water of a number of varnish components. H. A. Gardner and P. C. Holdt[47] have also given this matter some attention and have published a list of "drop numbers" in water for various oils and thinners. There would appear, however, to be no sort of agreement between the results obtained by these different investigators. This may be not altogether surprising when one remembers the variable character of some of these substances, but the observations of

[45] *J. Oil and Colour Chem. Assoc.*, 1920, **3**, 29.
[46] *Ibid.*, 1921, **4**, 129.
[47] *Circ.* 124, *Paint Manufrs. Assoc. U.S.*

W. C. Reynolds[48] are particularly interesting in this connexion. This author finds that a modification of the capillary method of measuring surface tension can be employed to measure interfacial tension to a much greater degree of accuracy than can be obtained by the use of the drop number method. By means of this new method of observation evidence may be obtained of chemical action or of changes in surface concentration which otherwise might be overlooked. Turpentine in contact with air undergoes oxidation so rapidly that the accurate measurement of its interfacial tension in contact with water is made very difficult; thus, four samples of the same turpentine, distilled under different conditions as regards access to air, gave values ranging from 10·2 to 34·2, although they all showed the same value, 27·2, for the surface tension to air. Moreover, the higher values very quickly fell on allowing the samples to stand in contact with air. After standing for 111 days in a bottle plugged with cotton wool a value of only 1·06 was obtained. The quantity of oxidation product producing this enormous difference is very small, and the more apparent properties of the turpentine remain unchanged. These remarkable results of Reynolds would appear to have considerable bearing upon the use of turpentine in varnishes.

Were our knowledge of surface energy relations more extensive it is probable that many problems concerning the permeability and water-absorbing power of varnish films would be more readily understood. R. S. Morrell[46] in continuation of his investigations on this subject has definitely established the fact that dry varnish or oil films act as semipermeable membranes in aqueous solutions of salts. Interesting conclusions have also been reached by this author regarding the relationship between the percentage of water absorbed by a dry varnish film and the proportions of resin, polymerised oil, linoxyn, and driers present in the film. In the main, the experience of the present writer is to confirm Morrell's conclusions, but there are a number of anomalies which require further elucidation. These would appear to be due largely to the fact that the water absorption as measured is usually, if not invariably, a composite quantity comprising not only the water dispersed throughout the varnish film, but also a layer of water enclosed between the varnish film and its support.[49] Quite probably there is a connexion between these two terms, to the extent that as water is absorbed into the film the adhesion between the film and its support becomes weakened, but on the other hand, they are probably not affected to the same degree by variable conditions, such as the thickness of the film, the nature and condition of the material to which the film is attached, and the rate of drying of

[48] *Chem. Soc. Trans.*, 1921, **119**, 460.
[49] H. H. Morgan, *J. Oil and Colour Chem. Assoc.*, 1921, **4**, 151.

the film. Further development along Morrell's line of attack should lead to interesting and valuable results.

Of quite common occurrence nowadays in varnish specifications is a test referring to the tendency of a dry varnish film to whiten when immersed in water. It is important therefore that the cause and nature of this whitening be better understood than it is at present. There seems to be no very definite connexion between the degree of whitening and the water absorption as measured by Morrell's method. This may possibly be due to the failure of Morrell's test to differentiate between "dispersed" water and "occluded" water, as mentioned above, or, again, it may be due to a difference in the form of the emulsion produced, owing to differences in the constitution of the varnish. As a result of a series of tests, E. G. Bloch [50] has concluded that there is no connexion between this whitening effect and the durability of a varnish. The fact that all the varnishes tested by Bloch cracked and perished after only 14 weeks' exposure would seem to indicate that his choice of varnishes was not a particularly suitable one. Nevertheless, the experience of R. S. Morrell [46] confirms the actual conclusion reached by Bloch in so far as "non-whitening" is, by itself, no criterion of durability. It is the opinion of the present writer that, in making this test an indication as to durability under normal conditions of exposure, less attention should be paid to temporary whitening and more attention to the intensity of the whiteness, to its degree of permanence after removal of the film from the water, and to any permanent injury to the film resulting from immersion. Morrell[46] has, however, put forward the suggestion that, if brittle varnishes be excluded, then the water-resisting power of elastic varnishes is a measure of their durability. To this end brittleness of a dried film is arbitrarily defined with respect to both time and temperature of drying and to power of resistance to fracture on bending. There is no doubt that amongst varnishes of the same type, and made on similar lines (the only differences being in the ratio gum-resin to oil), Morrell's method accurately differentiates as regards durability. But to be of wider application it is the present writer's opinion that other factors will have to be taken into consideration. It is just possible that more accurate predictions might be made if the method of differentiating between brittle and elastic varnishes were amplified somewhat on the lines of the kauri reduction test recommended long ago by American writers, and reconfirmed by them quite recently.[51] In the writer's opinion, however, the effects on durability of excess driers and of different degrees of polymerisation are not sufficiently indicated by the above tests.

[50] *Drugs, Oils and Paints*, 1921, **36**, 426.
[51] *U.S. Bureau of Standards Circ.* 103, 2nd Ed., Oct., 1921.

In connexion with brittleness tests mention may be made of some trials by H. A. Gardner[52] in which he measured, by means of paper-testing machines, the bursting strength and tensile strength of bond paper which had been varnished and dried; the same varnished papers were also exposed to weathering influences, but the results seem to be of little value. H. Wolff[53] has also described a method for testing the elasticity of varnish films. By means of a simple home-made device, the angle is measured at which fracture of the film occurs when the latter and its support (tinned iron, parchment, etc.) are gradually bent. The nature of the fracturing is also taken into account. With elastic varnishes the number of repeated bendings, backward and forward, is observed. The effects of thickness of film, number of coats, and other factors, on elasticity have been studied and are recorded. The same author has described an attrition test for varnish films.[54] A simple mechanical device is used in order to obtain a uniform pressure between the film and a "scrubber"; and hence the weight of film lost per unit area in unit time when "scrubbed" at constant pressure may be determined.

It is evident that there are wide differences of opinion as to the most important factors to be taken into consideration in predicting as to the durability of varnishes, and it seems necessary that many physical tests be made both on the dried film and on the varnish itself; moreover the results so obtained must be interpreted by a skilled varnish technologist.[55] It is possible that some chemical test regarding the nature and quantity of driers might be advantageous, though this is very doubtful. Much time has been spent in attempts to devise so-called accelerated weathering tests; also the effects produced by corrosive gases[56] and liquids[55] have frequently been put forward as affording evidence regarding durability under normal conditions of exposure. It is the writer's opinion, however, that little will be gained by such methods, and that there will be no real advance until more is known as to the relation between durability and the physico-chemical properties of the undried varnish. It is in this direction that knowledge is so badly needed.

There is very little to report in connexion with cellulose varnishes. R. O. Herzog, A. Hildesheimer, and F. Medicus[57] discuss in great detail the properties and manufacture of nitrocellulose lacquers. They have studied the influence of a large number of esters and

[52] *Circ.* 122, *Paint Manufrs. Assoc. U.S.*

[53] *Farben-Zeit.*, 1921, **26**, 2587; *J.*, 1921, 630A.

[54] *Ibid.*, 1921, **26**, 3111; *J.*, 1921, 742A.

[55] *See also* A. de Waele, *J. Oil and Colour Chem. Assoc.*, 1920, **3**, 75.

[56] H. Wolff, *Farben-Zeit.*, 1921, **26**, 1186; *J.*, 1921, 357A.

[57] *Z. angew. Chem.*, 1921, **34**, 57; *J.*, 1921, 228A.

other substances on various properties of the film, such as elasticity, water absorption, etc. A. Hildesheimer,[58] in a patent for the production of flexible lacquers from cellulose esters, describes the use of glycol esters of fatty acids of non-drying oils, the esters being prepared by the aid of catalysts such as Twitchell's reagent.

In 1918 a patent[59] was taken out for the production of varnishes "just as good as the more expensive gum varnishes" by the introduction of furfural into linseed oil rosinate varnishes, but C. Coffignier[60] has now shown that the furfural plays only the part of a solvent in the varnish—just like turpentine. Modern methods which have been adopted in America during the last few years for erecting and installing varnish-making factories are described, both by C. H. Jones[61] and by P. W. Webster.[62] The descriptions deal in particular with the question of recovery of fumes. M. Ragg[63] describes experiments to prove that when rosin and lead acetate are heated together at 110° C. a definite compound of "aceto-abietic acid" is formed. Hence, by analogy, he suggests that the slow-drying properties of linseed oil-rosin varnishes may be explained by the formation of similar complexes of the fatty and resin acids. The "combination" between lead acetate and rosin is undoubtedly a fact and is very curious, but the assumption of an "aceto-abietic acid" seems hardly justified. On the other hand H. Wolff and C. Dorn[64] claim to have isolated from a linseed oil-rosin varnish, crystals of a mixed resin and fatty acid glyceride corresponding to 2 mols. of palmitic acid and 1 mol. of resin acid.

An investigation by W. Flatt[65] on the relative speeds of drying of linseed oil boiled with lead, manganese, and cobalt driers respectively, confirms many previously published results bearing on this question. One point is brought out, however, which is perhaps not so well known as it should be, but one which is supported by the experience of the present writer, *viz.*, that the rate of increase in the time of drying with increasing temperature varies considerably with the nature of the drier. For normal boiled oils the rate of increase is greatest with cobalt and least with lead, though if excess driers be present the problem becomes more complicated. This aspect of the question has been dealt with by R. P. L. Britton when referring to the fact that excess of driers causes a retardation in the rate of drying. He states that this is only so when drying takes place at ordinary temperatures, and that above a certain

[58] G.P. 338,475 ; *J.*, 1921, 708A.
[59] F.P. 494,300.
[60] *Bull. Soc. Chim.*, 1920, **27**, 865 ; *J.*, 1921, 51A.
[61] *Chem. and Met. Eng.*, 1920, **23**, 771 ; *J.*, 1920, 791A.
[62] *Circ.* 135, *Paint Manufrs. Assoc. U.S.*
[63] *Farben-Zeit.*, 1921, **26**, 2335 ; *J.*, 1921, 552A.
[64] *Chem.-Zeit.*, 1921, **45**, 1086 ; *J.*, 1921, 857A.
[65] *Farben-Zeit.*, 1921, **26**, 1441 ; *J.*, 1921, 357A.

"critical temperature" the rate of acceleration becomes normal. H. Wolff and C. Dorn[66] confirm much that has been written concerning the nature of the "foots" obtained from boiled oils. Non-precipitation of lead foots with certain samples of boiled oil is attributed to the protective effect of colloidally-dispersed albuminoid matter, agitation of the oil during heating preventing that decrease in the degree of dispersion of the albuminoid material which is necessary for the coagulation of the latter.

Questions as to the nature of the glycerides present in drying oils and the mechanism of their oxidation in the absence of driers belong more strictly to the section on Oils, Fats, and Waxes. They are dealt with more fully under that section, and a brief reference only is made to them here. S. Coffey[67] has carried out some very interesting experiments whereby the "true oxygen absorptions" of linseed oil and of its fatty acids have been determined. This work may be regarded as a useful contribution to the study of the oxidation of linseed oil, but due caution must be observed in drawing any deductions therefrom concerning the drying of linseed oil films under normal conditions. Coffey himself draws attention to the complex nature of linoxyn, and states that it probably contains, among unchanged constituents of the oil, condensation products of those compounds which he has suggested are the primary oxidation products of linseed oil. Quite apart, however, from questions as to condensation, polymerisation, and gelation, it is most probable that even the purely chemical changes taking place during the drying of linseed oil films under normal conditions, bear little more than a superficial resemblance to the changes that occurred under the conditions of Coffey's experiments. Conditions of temperature, thickness of oil film, and the rate at which volatile products leave the film, probably all affect even the *modus operandi* of the reactions occurring during the oxidation of a complex natural product such as linseed oil. The experiments of R. S. Morrell[68] on the increase in "surface acidity" of a varnish film on exposure to air, though not strictly comparable, are not without bearing on this point. The part played by the glyceryl radicle needs to be much more closely investigated. This has been repeatedly pointed out by R. S. Morrell[68] and others. The possibility of olein taking part in the oxidation process has been ruled out by Coffey, and the effect of the presence of mixed glycerides, the presence of which has been indicated by Morrell and other investigators, has been neglected. A. Eibner,[69] in a recent paper discussing the causes

[66] *Farben-Zeit.*, 1921, **27**, 26; *J.*, 1921, 780A.

[67] *Chem. Soc. Trans.*, 1921, **119**, 1152, 1408; *J.*, 1921, 630A, 780A.

[68] *Third Report on Colloid Chemistry, Dept. of Sci. and Ind. Research*, 1920, 105.

[69] *Farben-Zeit.*, 1921, **26**, 2397; *J.*, 1921, 551A.

underlying the slowness of drying of abnormal samples of linseed oil, states that linseed oils "containing" even a large proportion of oleic acid, dry normally by virtue of this grouping being present as a mixed glyceride in combination with linolic and/or linolenic acid. The same author refers to the effect on the drying property of linseed oil by exposure to light, both during storage and during the process of ripening of the seed. P. Slansky,[70] however, does not agree with Eibner in this respect and states that linseed oil expressed and exposed to air in absence of light dries normally. In the same paper Slansky makes some very pertinent remarks on the subject of the changes that take place during the drying of linseed oil, and confirms much that has been published previously. He regards a determination of increase in weight on oxidation as of little value in determining drying power, as it takes no account of the physical change of coagulation. This author also draws attention to a certain similarity between the process of "oxidation by air" and "thickening by heat in absence of air" as applied to linseed oil.[71] In this connexion H. Wolff[72] has made the observation that if pieces of thin tissue paper soaked in linseed oil are pressed together so as to form a compact block, and allowed to dry, the outer layers consist chiefly of oxidised oil and the inner layers chiefly of polymerised oil. More prolonged drying diminished the degree of difference between the layers with respect to the proportion of oxidised fatty acids present. S. Coffey[73] has studied the thickening of linseed oil by heating it in sealed tubes at a temperature of 250° C. for periods of time up to 42 hours. His results confirm many conclusions reached by previous investigators. A marked rise in the viscosity-time curve at 21 hours coincides with similar, though less distinct, breaks in the sp. gr. and acid value curves.

Resins.

During some recent experiments carried out at Farnborough by the research department of the Air Ministry, aircraft propellers coated with Japanese lacquer were spun at high speed when under the influence of a water spray. The results showed that such coatings were far more durable under this severe treatment than any covering involving the use of ordinary varnishes or paints.[74] It is well known that Japanese lacquer hardens only when exposed to a moist atmosphere, and it is stated that the difficulty of application is a serious drawback to its use. The investigations of R. Majima and his collaborators therefore, begun in 1907, are

[70] *Z. angew. Chem.*, 1921, **34**, 86; *J.*, 1921, 817A.

[71] *See also* Morrell, Ref. 68.

[72] *Farben-Zeit.*, 1921, **26**, 2851; *J.*, 1921, 706A.

[73] *J.*, 1921, 19T.

[74] Private Communication.

particularly interesting. This work is not without bearing also on the subject of artificial resins, although at present the connexion may not be very apparent. Majima[75] in 1915 synthesised 2.3-dimethoxy-1-*n*-pentadecylbenzene, $(CH_3O)_2C_6H_3(CH_2)_{14}CH_3$, and showed it to be identical with hydro-urushiol dimethyl ether which he had previously obtained by reducing and methylating "urushiol," the chief ingredient of Japanese lac. R. Majima and G. Takayama[76] have now compared the phenomena observed on oxidising the monomethyl ether of urushiol with those observed when its lowest homologue, viz., 2-hydroxy-*m*-tolyl methyl ether, is similarly treated, and so concludes that the oxidation of hydro-urushiol yields derivatives of diphenoquinone.

In continuation of the work begun by F. Reinitzer in 1914, two important papers have been published relating to the composition of Siam benzoin. This substance was then shown to be a mixture of three colourless crystalline compounds, viz., benzoic acid, siaresinol, and lubanyl benzoate. The last-named substance, together with a number of its derivatives, have now been described by A. Zinke and J. Dzrimal,[77] and lubanyl benzoate has been given a constitutional formula consisting of a benzene nucleus having a hydroxyl group and a methoxyl group orientated in the *ortho*-position, together with the chain $CH:CH.CH_2.O.CO.C_6H_5$ situated in the *para*-position with respect to the OH group. When crude benzoin is warmed with dilute aqueous caustic soda a very sparingly soluble precipitate is obtained which can be readily crystallised from alcohol and which is stated by F. Reinitzer[78] to be the sodium salt of *a*-siaresinolic acid. The latter has the formula $C_{30}H_{48}O_4$, contains a carboxyl group, and is identical with siaresinol mentioned above.

Several papers bearing upon the vexed problem of the constitution of the resin acids have been published during the past year. Although much interesting and valuable information has accumulated respecting the relationships between abietic acid, retene, pinene, and so forth, much yet remains to be done before the constitution of the resin acids is established, whilst even the composition of colophony is still largely a matter for speculation. A. Grün[79] proposes a new constitutional formula containing a bridged linking for abietic acid, which formula not only explains its general behaviour but also accounts for its formation from pinene. A number of abietic and pimaric acids may be formed by the condensation of 2 molecules of pinene in different ways, and others again from camphene and fenchene. A. J. Virtanen[80] exhaustively reviews the literature of

[75] *Ber.*, 1915, **48**, 1606; *J.*, 1916, 128.

[76] *Ber.*, 1920, **53**, 1907; *J.*, 1920, 792A.

[77] *Monatsh.*, 1920, **41**, 423; *J.*, 1921, 153A.

[78] *Arch. Pharm.*, 1921, **259**, 60; *J.*, 1921, 277A.

[79] *Chem. Zentr.*, 1921, **92**, I., 496; *J.*, 1921, 311A.

[80] *Ber.*, 1920, **53**, 1880; *J.*, 1920, 792A.

the resin acids and describes the preparation and properties of several hydrogenated retenes, most of which are surprisingly stable towards permanganate. He expresses the view that all resin acids having the formula $C_{20}H_{30}O_2$ contain in their molecule a hydrogenated retene nucleus. O. Aschan[81] has isolated, from the less volatile fractions obtained by distilling pine oil in superheated steam, a new acid, $C_{20}H_{30}O_2$, belonging to the abietic series. This acid, which has been named pinabietic acid, is well characterised and crystalline; its rotatory power is affected to a remarkable degree by the nature of the solvent used, being strongly dextrorotatory in aromatic solvents and lævorotatory to an approximately equal degree in aliphatic solvents. From an extended study of the properties and general behaviour of this substance, A. J. Virtanen[82] has established definite relationships between Aschan's pinabietic acid, a new hydrocarbon pinabietene ($C_{19}H_{28}$), and the hydrocarbon retene. As a result, he has put forward a constitutional formula for pinabietic acid which is probably very near the truth, although the evidence is not sufficient to decide between several alternatives in which the differences are, however, of more or less a minor character. G. Dupont[83] has shown that it is possible to extract both *l*- and *d*-pimaric acids from the "gemme," or exuded resin, of the *Pinus maritima*, although under the acid treatment commonly used for the isolation of pimaric acid from this source, the lævo acid is usually changed to its dextro isomeride. O. Aschan[84] describes several members of a new series of acids which he has isolated from American colophony and which he has named colophenic acids. They have the generic formula $C_nH_{2n-10}O_4$. W. Fahrion,[85] however, recalls his own work on the autoxidation of colophony[86] in which he had described products of a peroxide nature having the formulæ $C_{20}H_{30}O_4$ and $C_{20}H_{30}O_6$, and states that Aschan's colophenic acid is apparently identical with his own oxyabietic acid. The methods of preparation employed by Aschan would seem to support Fahrion's contention, but, on the other hand, Aschan's compounds appear to be more stable than those described by Fahrion. In any case it is always difficult to decide whether compounds isolated from resins really represent original constituents or whether the latter have not undergone some change during the process of isolation.

P. Nicolardot and C. Coffignier[87] have described a simple mechanical device for determining the relative hardness of oil-varnish resins

[81] *Annalen*, 1921, **424**, 117, 133; *J.*, 1921, 594A.
[82] *Annalen*, 1921, **424**, 150; *J.*, 1921, 594A.
[83] *Comptes rend.*, 1921, **172**, 923, 1373; *J.*, 1921, 357A, 478A.
[84] *Ber.*, 1921, **54**, 867; *J.*, 1921, 439A.
[85] *Ber.*, 1921, **54**, 1944; *J.*, 1921, 780A.
[86] *Z. angew. Chem.*, 1907, 356, 361; *J.*, 1907, 264.
[87] *Chim. et Ind.*, 1921, **5**, 150; *J.*, 1921, 310A.

by measuring the diameter of the impression made by a weighted steel ball. The various resins have been classified according to the results obtained in this way, but in the opinion of the present writer the classification is not altogether satisfactory. In any case it is questionable as to how much value should be placed on the grading of oil-varnish resins according to the hardness of the raw material. An interesting contribution on the subject of hardened rosin and resin esters is made by A. Murray[88] who gives details regarding the method of manufacture of these products. As a result of various trials he concludes that copper acts as a polymerising catalyst on Congo copal, since only in aluminium vessels was he able to produce glycerin esters of low acid value from mixtures of Congo copal and rosin, containing large quantities of Congo copal. In connexion with the subject of hardened rosin and metallic rosinates, mention should be made here of two papers issued from the laboratory of H. A. Gardner. In one of these entitled "Lime for the Varnish Industry,"[89] suggestions are made as to what are the attributes of a high-grade lime best suited to the requirements of the varnish manufacturer. The use of a fully hydrated lime of low magnesian content is recommended. In the other paper referred to,[90] full details are given for the manufacture of such metallic rosinates (also of linoleates and tungates) as are commonly used in the paint and varnish industry; their properties and uses are also described.

Judged by the number of patents granted during the past year referring to the manufacture of synthetic resins, interest in this subject would appear to be maintained at the same pitch as that shown during the last few years. As far as can be judged by the patent literature, however, no very striking advance seems to have been made. Many of the patents[91] refer to the phenol-aldehydic condensation products, and either introduce a new condensing agent or specify some plastic, filler, or other material for the purpose of producing a tougher or less brittle product. It is difficult to detect any advantages that might accrue from the working of these patents over the older ones, with the exception of such as might arise from economic considerations. Very few new patents[92] have appeared that deal with resins of the coumarone type, and none

[88] *Chem. and Met. Eng.*, 1921, **25**, 473; *J.*, 1921, 741A.

[89] *Circ.* 113, *Paint Manufrs. Assoc. U.S.*

[90] *Circ.* 120, *Paint Manufrs. Assoc. U.S.*

[91] Vickers, Ltd., E.P. 154,6[illegible], 158,447, 160,258; *J.*, 1921, 91A, 228A, 358A. L. A. Jaloustre and others, E.P. 139,147, 138,061; *J.*, 1921, 122A. Damard Lacquer Co., E.P. 169,347; *J.*, 1921, 780A. Resan Kunstharzerzeugungsge.s, E.P. 130,608; *J.*, 1921, 666A.

[92] The Barrett Co., E.P. 166,818, U.S.P. 1,360,665; *J.*, 1921, 708A, 91A. A. L. Tannehill, U.S.P. 1,389,791; *J.*, 1921, 781A. Rütgerswerke A.-G., G.P. 32[illegible]575; *J.*, 1921, 19A.

contains any outstanding feature. Several patents occur in which condensations are described involving the use of naphthalenes—*e.g.*, the Akt.-Ges. für Anilin-Fabr.[93] has taken out four patents for the manufacture of varnish-resins from formaldehyde and either halogenated or hydrogenated naphthalenes. The Bayer Co.[94] condenses naphthalene with dichloroxylene or similar halogenated compound. The Badische Co.[95] states that xylol and ethylene chloride can be made to react in the presence of aluminium chloride to give a solid resin free from chlorine. The same company has been granted two patents[96] describing the use of cyclohexanone as a resin-producing substance.

The fact that resinous substances may be produced as a result of these various condensations etc. is very interesting, but the varnish chemist is inclined to be suspicious of "synthetic" substances concerning the constitution of which little is known. That he knows little about the composition of the natural resins is, of course, largely compensated for by the accumulated experience of generations of varnish makers. Scientific investigation as to the changes which take place during resinification is badly needed. L. H. Baekeland[97] has done much on this subject in connexion with phenolic condensation products, and a further study on phenolic hexamethylenetetramine compounds by M. Harvey and L. H. Baekeland[98] has been published during the past year. H. Lebach[99] pointed out in 1909 that whenever ammonia is used in the bakelite reaction, hexamethylenetetramine-triphenol is formed in the first stages of the process, and that under the action of heat this product resinifies with the elimination of ammonia. By using carefully purified cresols, and paying strict attention to temperature, Harvey and Baekeland[98] have succeeded in isolating crystalline compounds of hexamethylenetetramine with *o*-, *m*-, and *p*-cresol, respectively, contrary to the results of H. Moschatos and B. Tollens[100] who were unable to prepare such products. The corresponding compounds of quinol, of resorcinol, and of carvacrol, have also been isolated. The *m*-cresol, *p*-cresol, and carvacrol compounds have no true melting point, but resinify when heated at their point of liquefaction. The o-cresol, quinol, and resorcinol compounds, on the other hand, partly sublime and partly char on heating, showing very little signs of melting. These two different types of change, which occur on heating, seem to be

[93] G.P. 305,575, 332,334, 332,391, 334,710; *J.*, 1921, 439A, 358A, 479A.

[94] G.P. 302,521; *J.*, 1921, 708A.

[95] G.P. 326,729; *J.*, 1921, 142A.

[96] G.P. 337,993, 339,107; *J.*, 1921, 631A, 742A.

[97] *J. Ind. Eng. Chem.*, 1913, **5**, 506.

[98] *J. Ind. Eng. Chem.*, 1921, **13**, 135; *J.*, 1921, 187A.

[99] *Cf. J.*, 1913, 559.

[100] *Annalen*, 1893, **272**, 271.

governed by the ratio of the number of molecules of phenol to one molecule of hexamethylenetetramine in the compound, but as to what limits this ratio there is as yet no clue. Incidentally, the suggestion is made that the constitution generally accepted for hexamethylenetetramine is incorrect. A connexion between resinification and chemical constitution is suggested by W. Herzog,[101] who states that the grouping—N : C : N—is a typical resinophore group, being characteristic of a whole class of substances which readily undergo polymerisation to resins. This is illustrated by the case of *sym.*-diphenylthiocarbamide, which, when dissolved in aniline and heated at boiling point for forty hours, yielded a clear amber-like resin, soluble in benzene, fatty oils, and in turpentine. Hydrogen sulphide is first evolved and the resulting carbo-di-imide polymerises. The same author describes the preparation of a resin resembling colophony, by heating formaldehyde with benzylaniline, using hydrochloric acid as a catalyst.[102]

European patents for the technical preparation of furfural from cellulosic material were taken out so long ago as 1912 and 1913. In 1916 J. Meunier[103] described the production of synthetic varnish resins by the condensation of furfural with various amines or ketones, and in 1918 E. Beckmann and E. Dehn[104] showed that hard resins similar to the bakelite products could be obtained by the condensation of furfural with phenols. So far very little appears to have been heard about these various processes, but they now seem to be attracting some attention in America[105] due, no doubt, to the discovery by K. P. Monroe[106] that corncob pentosan affords a source from which furfural may be easily and cheaply manufactured in large quantities. It will be interesting to see whether this promised source of cheap furfural will affect the production of synthetic resins, either as regards cost or as regards quality.

The use of varnishes made from the bakelite type of synthetic resin is increasing, chiefly, however, in those cases where high electrical or chemical resistance is required. It is unfortunate that stoving is necessary in order to obtain the requisite power of resistance. With this exception, synthetic resins do not appear to be used to any appreciable extent in England for the manufacture of lacquers or varnishes. In the opinion of the writer it seems rather a pity that so much time and energy are being devoted

[101] *Oesterr. Chem.-Zeit.*, 1921, **24**, 76; *J.*, 1921, 478A.

[102] *Oesterr. Chem.-Zeit.*, 1921, **24**, 16; *J.*, 1921, 187A.

[103] *Mat. Grasses*, 1916, **9**, 4516.

[104] *Sitzungsber. Preuss. Akad. Wiss.*, 1918, 1201; *J.*, 1920, 577A.

[105] *See* G. H. Mains and M. Phillips, *Chem. and Met. Eng.*, 1921, **24**, 661; *J.*, 1921, 357A.

[106] *J. Ind. Eng. Chem.*, 1921, **13**, 133; *J.*, 1921, 194A.

to the possible production of synthetic resins merely to replace the natural "gum" in oil varnishes. A varnish is needed which, when applied and air-dried in the ordinary way, will yield a film far more durable and resistant to chemical and mechanical forces than any varnish yet made, or that is likely to be made, from linseed oil, tung oil, etc. The type towards which investigators should strive would seem to be a product somewhat after the nature of Japanese lac; preferably also a material which could be applied in the fluid condition, at ordinary temperature, without the use of volatile solvent.

INDIA-RUBBER.

By B. D. Porritt, M.Sc., F.I.C., F.R.S.E.,

Director of Research, Research Association of British Rubber and Tyre Manufacturers.

The period under review has been one of exceptional difficulty in practically every industry, and neither the producer nor the manufacturer of rubber has escaped the effects of the prevailing trade depression.

Rubber—one of the few commodities which did not rise in price during the war—steadily depreciated in value from February, 1920, until June, 1921, when smoked plantation sheet could be purchased at the unprecedented price of 7d. per lb. As the average cost of production is at present in the neighbourhood of 15d. per lb.[1] the position of the rubber grower has obviously not been an enviable one; and, so important has the plantation industry become to the prosperity of the Empire, that a Government committee has been appointed recently to consider its present difficulties.[2]

In the case of the manufacturer, the low price of raw rubber has proved insufficient to compensate for other difficulties with which he has had to contend, particularly the remarkable fluctuation in the price of cotton and the prejudicial effect on home and export demands resulting from trade depression, foreign competition, and abnormal rates of exchange.

These adverse conditions have rendered it imperative for those responsible for the management of both branches of the industry to make every effort to reduce costs of production, and to popularise and find new uses for rubber.

In this latter direction the lead has been taken by the Rubber Growers' Association, in the institution of a public competition for new and extended uses for rubber, and, although this enterprise does not appear to have produced the results anticipated[3] it has at least done much to direct popular attention to the many purposes for which rubber is suitable.

It is evident, moreover, that increasing importance is being attached to the value of scientific control and research, in connexion

[1] *India Rubber J.*, 1921, 62, 691.
[2] *Rubber Age*, 1921, 2, 455.
[3] *India Rubber J.*, 1921, 62, 619; *J.*, 1921, 498R.

with both the production and the manufacture of rubber. The study of the botanical and mycological problems of the *Hevea Brasiliensis* has been undertaken recently by Prof. J. B. Farmer at the Imperial College of Science, for which purpose generous support has been provided by rubber growers,[4] whilst the existing arrangements for research on the estates in Ceylon and the Federated Malay States are to be reorganised and extended.[5] At home the Research Association established by the trade under the Government scheme for the encouragement of technical research is steadily developing its work,[6] and is now engaged in equipping new laboratories, adequate for its requirements, at Croydon. In this connexion it is interesting to note a recent proposal to establish a similar co-operative research laboratory in the United States.[7]

The importance of technical education, moreover, has not been overlooked, and the existing facilities have been extended by the introduction of day and evening courses of instruction at the Northern Polytechnic, in connexion with which a scheme of post-graduate research scholarships has been instituted.

A further stimulus to research work was provided by the scientific conference which took place in connexion with the International Rubber Exhibition held in London during July. This meeting, the first since the outbreak of war, was attended by many important foreign workers on the problems relating to the production and manufacture of rubber, and presented a welcome opportunity for discussion and the interchange of ideas.

Although no new discovery of outstanding interest has occurred during the year, very material progress has to be recorded—more particularly in connexion with the elucidation of the action of vulcanisation accelerators and the effects produced by these and other ingredients on the physical properties of rubber. The notable advance made in these directions since 1914 was the outstanding impression left on the minds of those attending the Rubber Exhibition Conference, and the day seems to be approaching when vulcanisation will no longer be a mysterious change susceptible only to somewhat empirical control.

Statistics.

The world-wide commercial depression has naturally resulted in a set-back to the steady increase in the demand for raw rubber, the production of which during the last ten years has practically doubled every four years.

[4] *Bull. R.G.A.*, 1921, **3**, 115.

[5] *Ibid.*, 1921, **3**, 113.

[6] *Annual Report of the Department of Scientific and Industrial Research*, 1920–21, 29.

[7] *India Rubber World*, 1921, **65**, 31.

The fact that, for the time at least, the supply had exceeded the demand was realised in 1920 by the majority of British producers, and a restriction scheme proposed by the Rubber Growers' Association for a 25% reduction in output was generally adopted by the estates. Negotiations with a view to securing the adoption of this proposal by the Dutch rubber planters have proved unsuccessful,[8] whilst the Colonial Office declined to introduce legislation imposing a 50% reduction of output in Malaya.[9] A proposal that the members of the Rubber Growers' Association should continue the voluntary 25% reduction scheme for a further period of six months failed to secure the necessary support,[10] and consequently the regulation of output during 1922 has been left solely to the operation of economic laws.

This arrangement, assisted by the effects of low prices and increased cost of labour, has resulted in a marked reduction in the output for 1921, which is estimated at 245,000 tons, as compared with 368,000 and 339,000 tons for 1920 and 1919 respectively.[11]

The potential output of rubber, however, is already increasing, that for 1922 being estimated at 400,000 tons,[12] whilst the existing plantations alone are deemed capable of yielding at the rate of 500,000 tons per annum within a comparatively short period. This would seem probable from the following statistics.[13]

	Area planted 1st Jan., 1920. Acres.	Area producing Acres.
Malaya	1,750,000	1,250,000
Ceylon	398,000	267,000
S. India	65,000	43,000
Burma	45,000	17,500
Netherlands' India	885,000	570,000
Borneo and Sarawak	50,000	30,000
Other Countries	130,000	60,000
Total	3,323,000	2,237,000

To ensure the future prosperity of the plantation industry, therefore, a steady and rapid increase in the world's consumption of raw rubber must follow the return to normal conditions, since for the last three years the demand has remained practically stationary at about 300,000 tons per annum, resulting in the accumulation of a surplus stock variously estimated to amount to between 70,000 and 90,000 at the end of 1920.

[8] *India Rubber J.*, 1921, **62**, 458.
[9] *Bull. R.G.A.*, 1921, **3**, 198.
[10] *Ibid.*, 1921, **3**, 434, 495.
[11] *India Rubber J.*, 1921, **61**, 429.
[12] *Bull. R.G.A.*, 1921, **3**, 257.
[13] *Ibid.*, 1921, **3**, 8.

The most likely outlet for an increase in production would appear to exist in countries in which the demand for rubber goods is at present slight, as illustrated by the following figures for per capita consumption :—United States, 4·15 ; Great Britain, 1·48 ; France, 1·00 ; Italy, 0·50 ; Japan, 0·35.

Any marked increase in the consumption of raw rubber would, moreover, seem most likely to depend upon the general development of motor transport, which has attained remarkable proportions in the United States,[14] as may be judged from the fact that the number of motor vehicles registered increased from 1,254,971 in 1913 to 9,211,295 in 1920.[15] As the world's total is estimated at 10,922,278 vehicles, it would appear that the United States' proportion amounts to no less than 83%, or, in other words, there are five times as many cars in use in that country as in all the rest of the world.

Whilst special circumstances have no doubt contributed to the present preponderating position of the United States as a user of motor vehicles and tyres, it would appear reasonable to anticipate that the gradual development of motor transport in other countries will in time equalise the present disproportion and provide a market for the whole output of the existing plantations. Such development, however, must be conditional upon adequate and cheap supplies of motor fuel, and the continued prosperity of the plantation industry will therefore, to no small degree, depend upon those of petroleum and benzene, and upon the measure of success which attends the search for petrol substitutes.[16]

Production of Raw Rubber.

The existing adverse conditions in the rubber market have naturally accentuated the importance of making every possible reduction in the cost of production of plantation rubber, and for this reason increased attention is being given to the well-being of the tree and the factors which govern the yield of latex. It is evident, however, that any investigations with the object of improving, from the point of view of the planter, the yield of rubber or the processes of preparation, should also take into account the interests of the consumer, and, for this reason, the recent formation of a liaison committee between the Rubber Growers' Association and the British Rubber and Tyre Manufacturers' Research Association, and the inclusion of rubber manufacturers on the Ceylon Research

[14] *India Rubber World*, 1921, **64**, 728.

[15] *Ibid.*, 1921, **63**, 411.

[16] *Report of the Committee for Scientific and Industrial Research*, 1920–21, 43. "Power Alcohol, its Production and Utilisation": G. W. Monier-Williams. Hodder & Stoughton.

Advisory Committee[17] are to be welcomed. It is a matter for regret that in the past outward appearance has been the factor determining the market price of plantation rubber, as estate managers have concentrated upon turning out a product of good appearance, without regard to the more important questions of uniformity of vulcanisation and physical properties.[18] As a result, although plantation rubber now represents 90% of the world's supply, it cannot yet be described as ideal from the standpoint of the consumer, who still prefers to use fine hard Para for certain special purposes, of which the manufacture of elastic thread may be given as an example. One of the reasons for this preference is, no doubt, that of uniformity of vulcanising properties, in which respect the early supplies of plantation rubber were seriously deficient.

Since 1914 a large amount of work has been carried out in order to remove this ground for criticism, and as a result it is now possible, by careful attention to the methods of preparation, to produce a reasonably uniform product.

According to de Vries,[19] the average variation in the rate of cure for smoked sheet from 150 estates in Java is now about 11%; whilst individual plantations, working on standardised methods, can reduce this figure to about 2·5%. These results, however, are more probably an indication of the degree of uniformity which is possible than an index of the general quality of the plantation rubber on the market, since this includes not only the output of large, carefully supervised estates, but that of many small ones paying little regard to scientific methods.[20]

Until such time, therefore, as uniformity of "cure" is accompanied by an enhanced price, there would seem to be little incentive for general improvement. Meanwhile, a more extensive adoption of identification marks on the sheets of rubber would appear desirable on the part of those estates producing a reasonably uniform product.

Whilst variability in vulcanising properties has been the main difficulty experienced by manufacturers in dealing with plantation rubber, this has not been the only ground for criticism.

The existence of variations in the amount of mastication necessary to secure the degree of plasticity required for various factory processes has been suspected for some time, and recently some preliminary investigations into the problem have been published by H. P. Stevens.[21]

[17] *Bull. R.G.A.*, 1921, 3, 114.

[18] O. de Vries, *Rubber Age*, 1921, 2, 105.

[19] *Ibid.*, 1921, 2, 360.

[20] In the Federated Malay States 409,026 acres are represented by holdings of less than 100 acres each (*India Rubber J.*, 1921, 62, 30).

[21] *Bull. R.G.A.*, 1921, 3, 340.

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[15] *Ibid.*, 1921, **63**, 411.

[16] *Report of the Committee for Scientific and Industrial Research*, 1920–21, 43. "Power Alcohol, its Production and Utilisation": G. W. Monier-Williams. Hodder & Stoughton.

It is unfortunate that the great variation in the latex-yielding characteristics of individual trees was not recognised at an earlier date,[26] since, owing to the comparatively slow development of the trees, a considerable period must elapse before any definite information can result from experiments on selective propagation, which have produced such satisfactory results in the case of the cinchona and indigo industries. Meanwhile, any improvement on the estates must be mainly confined to the selection of poor trees for removal when thinning-out is necessary.[27]

A number of papers have appeared during the year, dealing with various aspects of the coagulation of latex, including one by G. Vernet,[28] reviewing the general theory of the process. The effect of substituting serum for water to dilute the latex has been studied by O. de Vries,[29] and it has been shown that this practice may tend to produce a non-uniform product, on account of the gradual increase in the amount of the nitrogenous constituents, the decomposition products of which constitute the natural vulcanisation accelerators present in raw rubber. W. Spoon [30] has amplified the earlier observation of Eaton, that the use of brackish tidal river water for latex dilution affects the quality of the rubber. It is found that the presence of as little as 12% of sea water is sufficient to produce an appreciable change in both the strength and the rate of cure of smoked sheet, although in the case of crêpe the proportion may be increased to 28% before any detrimental effect becomes apparent. De Vries and Spoon have, in conjunction, published the results of an investigation into the Ileken-Down process for the preparation of rubber,[31] which is based on the spontaneous coagulation of the latex in the presence of a mixture of alcohol and fusel oil,[32] and is claimed to give a yield of 5% to 15% in excess of that obtained by the usual process. The results, however, do not point to any material difference in the yield, whilst the product was found to possess the normal properties of a slow-vulcanising rubber.

The investigations into the effects produced by variations in the method of preparation on the ageing qualities of the rubber have been continued by O. de Vries and H. J. Hellendoorn,[33] and their results indicate that reasonable variations in the method of coagulation and the treatment of the coagulum do not appreciably

[26] See *Ann. Repts.*, 1920, **5**, 334.

[27] R. M. Richards, *Rubber Age*, 1921, **2**, 77. C. A. Gehlsen, *Archief*, 1921, **5**, 453.

[28] *Bull. Caoutchouc Inst. Colon. de Marseille*, 1919, 107; *J.*, 1921, 188A.

[29] *Comm. Central Rubber Stat. Buitenzorg*, 1921, No. 27; *J.*, 1921, 631A.

[30] *Ibid.*, 1921, No. 25; *J.*, 1921, 399A.

[31] *Ibid.*, 1921, No. 27; *J.*, 1921, 631A.

[32] E.P. 8487 of 1915; *J.*, 1916, 854.

[33] *Comm. Central Rubber Stat. Buitenzorg*, 1920, **4**, No. 24; *J.*, 1921, 123A.

affect the keeping properties of the rubber. It would appear that fast-curing rubbers tend to show a decrease in the rate of vulcanisation on keeping, whilst with slow-vulcanising samples the change is in the opposite direction. The general effect of ageing therefore would seem to be in the direction of producing a greater degree of uniformity.[34] In a recent paper [35] G. Bruni and C. Pelizzola drew attention to the presence of manganese in samples of rubber which developed tackiness on keeping, and put forward the suggestion that colloidal manganese oxide, acting as an oxidation catalyst, may be the causative agent in certain cases in which deterioration takes place on keeping. It was found, however, that samples of African rubbers, which are notoriously prone to develop tackiness, were free from manganese, and, according to A. Dubosc,[36] with this class of rubber the effect is to be attributed to the presence of sodium chloride.

During recent years the drying of rubber has received considerable attention, more particularly from the point of view of the manufacturer; the underlying principle of the various new systems advocated appears to consist in reducing or eliminating the oxygen normally present in the process. In the first,[37] the air present in the drying chamber is first displaced with steam, and the removal of moisture is subsequently completed *in vacuo*; whilst in the second [38] an indifferent atmosphere is obtained by the use of purified flue gases.

The remaining method, known as the "Hunter-dry kiln process,"[39] has recently attracted considerable attention as the result of an experimental plant shown in operation at the Rubber Exhibition, and is claimed to have been largely adopted by manufacturers in the United States. By this process the drying is carried out in a heated chamber through which a current of air containing a high percentage of water vapour is circulated.

It is, however, too early to form any conclusion as to whether these processes offer any advantages over the methods of drying at present in use, and the same applies to a proposal to carry out the milling of rubber in the absence of oxygen.[40]

It is interesting to notice in conclusion a recent suggestion that direct use should be made of latex for the purpose of introducing a proportion of rubber into paper as a binding agent.[41] This proposal

[34] H. P. Stevens, *Bull. R.G.A.*, 1921, **3**, 291; O. de Vries, *Comm. Central Rubber Stat., Buitenzorg*, 1921, No. 25; *J.*, 1921, 400A.

[35] *India Rubber J.*, 1921, **62**, 101; *J.*, 1921, 5F3A.

[36] *India Rubber World*, 1921, **64**, 897.

[37] J. V. Worthington and A. W. T. Hyde, E.P. 150,043; *J.*, 1920, 698A.

[38] A. G. Metzler und Co., G.P. 332,974; *J.*, 1921, 440A.

[39] E.P. 138,915; *J.*, 1921, 92A.

[40] J. Porzel, E.P. 124,887; *J.*, 1921, 400A.

[41] F. Kaye, E.P. 167,935; *J.*, 1921, 690A.

recalls some of the early experiments of Goodyear and Hancock, and would seem to hold out most prospect of success in tropical countries, in which abundant supplies of suitable fibres and latex are to be found side by side.

VULCANISATION.

The last two annual reports have indicated clearly that this important subject has of late been receiving marked attention from scientific workers, and during 1921 numerous papers dealing with various aspects of vulcanisation have appeared, of which some of the most important will be discussed later under the heading of accelerators.

The investigation of the remarkable reaction discovered by S. J. Peachey,[42] by which vulcanisation is effected in the cold by the nascent sulphur formed as a result of the interaction of hydrogen sulphide and sulphur dioxide, has been continued, and patents have been taken out claiming the use of the reactive gases under pressure,[43] and the application of the process to compounding ingredients liable to be adversely affected by heating.[44]

The priority of Peachey's claim has been questioned by A. Dubosc,[45] who has drawn attention to the fact that some time previously he put forward the theory that the reaction taking place during vulcanisation in the presence of accelerators is due to interaction between the sulphur, resins, and bases yielding colloidal sulphur as a result of the formation and interaction of hydrogen sulphide and sulphur dioxide.[46] However, it does not seem to have occurred to Dubosc to subject this theory to experimental proof by introducing the gases from an outside source, and consequently his paper can scarcely be held to anticipate the discovery that, not only does vulcanisation result under these conditions, but that the change takes place at ordinary temperature.[47]

Arising from the study of accelerators, another process has been suggested recently by G. Bruni,[48] for effecting vulcanisation by means of sulphur without the application of heat. This method depends on the formation *in situ* of thiocarbanilide or other disubstituted aromatic thiourea by the action of carbon bisulphide on an aromatic amine incorporated in the rubber with a proportion of zinc or other metallic oxide. An example is quoted in which a mixing containing 100 parts of rubber, 8 of sulphur, 20 of zinc

[42] *Ann. Repts.*, 1919, **4**, 328 ; 1920, **5**, 332.
[43] S. J. Peachey, E.P. 162,429 ; *J.*, 1921, 439A.
[44] S. J. Peachey and A. Skipsey, E.P. 160,499 ; *J.*, 1921, 358A.
[45] *India Rubber J.*, 1921, **61**, 177 ; *J.*, 1921, 58T.
[46] *Ann. Repts.*, 1919, **4**, 329.
[47] S. J. Peachey, *India Rubber J.*, 1921, **61**, 163 ;
[48] *Giorn. Chim. Ind. Appl.*, 1921, **3**, 196 ; *J.*, 1921, 520A.

oxide, and 6 of aniline is vulcanised at ordinary temperatures by exposure to the vapour of carbon bisulphide.

In this connexion attention may be drawn to the discovery, dealt with later, that certain organic disulphides are capable of effecting vulcanisation rapidly without the presence of extraneous sulphur.

The experiments on the relative activity of various allotropic forms of sulphur as vulcanising agents have been continued by D. F. Twiss,[49] and in conjunction with F. Thomas some further results have been published.[50] By the use of an accelerator it was found possible to compare the efficiency of insoluble ($S\mu$) and soluble sulphur ($S\lambda$) at temperatures between 98° and 118° C., and, by the substitution of a synthetic dimethylbutadiene rubber for the natural product, to obtain a further series of results between 168° and 188° C., the degree of vulcanisation in the latter case being based on determinations of combined sulphur, and not on physical properties. Although the results obtained indicate that insoluble sulphur is somewhat less active than the other form, the outstanding conclusion is not so much the existence of this difference as the relatively equal efficiency of the several allotropic forms of sulphur as vulcanising agents.

Probably as a result of the convenient method discovered by Peachey, attention has been re-directed to the vulcanisation of rubber in solution, which had been effected by several earlier investigators.[51]

It has been found by H. P. Stevens [52] that if raw rubber containing 10% of sulphur be dissolved in benzene and the solution heated in a closed vessel under pressure, there results, according to the degree and duration of the heating and the concentration of the solution, either a viscous liquid or a homogeneous gel of vulcanised rubber, either of which, on the evaporation of the solvent, yields a film of vulcanised rubber which cannot be re-dissolved. The rate of vulcanisation was found to depend upon the nature of the solvent and the proportion of rubber present in the solution; for example, 10 grams of rubber in 100 c.c. of benzene was found to require twice the time necessary for the vulcanisation of the corresponding dry mixing at the same temperature. The solutions of vulcanised rubber obtained in this way appear to be very susceptible to the influence of light, which tends to convert them into gels, these, on storage in the dark, again reverting to the sol form.

[49] *Ann. Repts.*, 1919, 4, 327.

[50] *J.*, 1921, 48T.

[51] E. Stern, *J.*, 1909, 1050. F. W. Hinrichsen and F. Kindscher, *J.*, 1910, 891; G. Bernstein, *J.*, 1912, 1087. A. Helbronner and G. Bernstein *J.*, 1914, 653. B. D. Porritt, *Rubber Industry*, 1914, 168.

[52] *J.*, 1921, 186T.

The success of the suggested technical application of these observations [53] must largely depend upon the possibility of preparing reasonably concentrated solutions of vulcanised rubber, which do not change rapidly during use into intractable gels.

The properties of solutions vulcanised with sulphur monochloride, hydrogen persulphide, and trinitrobenzene have also been examined by Stevens, whilst independently the same field has been explored by M. Le Blanc and M. Kröger,[54] who have studied, in addition to the ordinary hot and cold methods, the Peachey process and the effects introduced by the presence of accelerators.

The results obtained by the various workers appear to be in general agreement, it being found that the solutions prepared by heating with sulphur show less tendency to gel formation if the rubber has previously been well masticated or heated, being in this respect superior to those vulcanised with sulphur chloride, which, judged by the writer's experience, are too unstable to be of any technical interest. In the case of gels prepared by the latter method, two types of the syneresis phenomenon are exhibited. When a high proportion of sulphur chloride has been used a gradual shrinkage takes place, the liquor expelled containing little or no rubber; whilst with smaller proportions of the vulcanising agent complete or partial transformation into the sol form occurs, with the separation of a solid deposit containing a high proportion of sulphur. In the case of the gels prepared by the action of sulphur and heat, syneresis of the first type only has been observed, and that only as a result of exposure to light.

It is noteworthy that all those who have recently investigated the formation of vulcanised rubber solutions have found that, contrary to what might be expected, the viscosity of the solution decreases as a result of the treatment, and an analogous change in viscosity is suspected to occur during the preparation of rubber gels by the action of light on solutions in the absence of oxygen.[55]

The suggestion of Le Blanc and Kröger that vulcanisation in solution may provide a simple and convenient method for the examination of accelerators is of considerable interest, it being stated that the effect of accelerators generally is to lower the viscosity of the rubber solution, and that, by a study of the syneresis and gel formation phenomena, it is possible to make quantitative comparisons of the influence of various accelerators.

From some work carried out by the writer, it would seem that both nitrosodimethylaniline and thiocarbanilide certainly reduce the viscosity markedly on heating for a few hours at 95° C., but the experiments showed that the presence or absence of sulphur

[53] H. P. Stevens, E.P. 164,770; *J.*, 1921, 553A.

[54] *Z. Elektrochem.*, 1921, 27, 335; *J.*, 1921, 667A.

[55] B. D. Porritt, *Rubber Age*, 1921, 1, 447.

in the rubber solution made little difference in the effects produced.

The results of further work on this subject will therefore be awaited with considerable interest. The development in our knowledge of the vulcanisation process which has taken place in recent years has re-directed attention to the pioneer work of Goodyear and Hancock, whose independent discoveries have for some eighty years formed the basis of the technique of the rubber industry. The long correspondence which has appeared in the technical press [56] regarding the relative merits of the discoveries of these remarkable men does not, however, appear to disclose any new facts or warrant any modification in the view that Goodyear was the first to prepare specimens of vulcanised rubber by the use of sulphur in conjunction with white lead, and that Hancock subsequently discovered that heating with sulphur alone would effect the change if air were excluded during the treatment.[57]

Accelerators.

The importance of accelerators of vulcanisation has been recognised from the early days of the industry, and it is to the accidental use by Goodyear of white lead in conjunction with sulphur that the discovery of vulcanisation has to be attributed. As the last few years have seen the introduction of many new and powerful compounds, compared with the simple inorganic bases formerly employed, it may be well to point out that the importance of such substances to the technologist depends, not so much on the actual saving of time which may be secured by their use, as on the provision of a convenient means by which rubber mixings may be modified to meet special conditions of manufacture and usage. It has to be remembered also that many rubber articles, such, for example, as buffers and solid tyres, owing to their size and thickness, must be heated up slowly to ensure uniform vulcanisation, whilst a considerable amount of heating takes place in certain processes of manufacture, during which premature vulcanisation would be fatal. Consequently the use of powerful accelerators calls for considerable caution, and renders indispensable special precautions for the accurate control of vulcanisation.

The development of the organic accelerator may be said to date from the time when the synthesis of rubber and the variation of the natural product began to attract the attention of scientific workers.

A large number of substances are now known to act as accelerators of vulcanisation, and these may be divided into the following three classes: (*a*) Organic and inorganic bases; (*b*) Aromatic

[56] *India Rubber J.*, 1921, **61**, 72, 181, 710, 742A, 782, 886, 1226; **62**, 27, 128.

[57] B. D. Porritt, *J. Roy. Soc. Arts*, 1919, **67**, 252.

nitroso compounds ; (*c*) Sulphur compounds containing the groups S : C·S- or -S·C·S'.

It was early recognised that other agencies were operative in vulcanisation besides sulphur and the accelerator, it having been noticed by L. E. Weber [58] and H. P. Stevens [59] that the removal of the natural resins was prejudicial to the action of litharge. Moreover, technical use soon showed that many of the organic accelerators required the presence of a small proportion of zinc oxide in the mixing before they could exert their full effect.

Until recently no adequate explanation had been put forward for these facts, although it has been suspected for some time that the active substance was not the accelerator, but some compound formed as a result of its interaction with the sulphur.

This suggestion has been put forward in various forms by Dubosc, Ostromyslenski, Kratz, Flower, and Coolidge, and by Scott and Bedford, besides being, the basis of two patents.[60]

A. Dubosc[61] assumes that the chief agent in promoting vulcanisation is thiocyanic acid. There is, however, no evidence in support of this theory beyond the observation of B. D. W. Luff [62] that this compound can be detected in pure mixings in which hexamethylenetetramine has been used, and it fails, moreover, to explain the action of accelerators which contain no nitrogen.

The more generally accepted view is that the reaction between accelerators and sulphur consists in the formation of unstable polysulphides which function as sulphur carriers.

I. Ostromyslenski[63] suggests that amines react with sulphur to form compounds of the thiozonide type, R·NH·S·S·S·NHR, by the loss of H_2S ; whilst Kratz, Flower, and Coolidge[64] assume the transient formation of an unstable pentavalent nitrogen addition compound $R{\cdot}NH_2{:}S$.

According to W. Scott and C. W. Bedford,[65] however, formation of polysulphides of the type $RNH_3.SH : S$ takes place ; in the case of an amine, a hydrosulphide is first formed by the addition of hydrogen sulphide resulting from the interaction of resins, protein, or the amine itself, and sulphur. On this assumption they classify accelerators—excluding those of the nitroso type—into two groups : (*a*) Hydrogen sulphide-polysulphide compounds ; (*b*) Carbo-sulphydryl polysulphide compounds. The first class

[58] *J.*, 1912, 888.

[59] *J.*, 1912, 1099.

[60] S. J. Peachey, E.P. 113,570 ; *J.*, 1918, 216A. Goodyear Tire and Rubber Co., E.P. 130,857 ; *J.*, 1919, 731A.

[61] *India Rubber World*, 1919, **59**, 248.

[62] *Rubber Age*, 1921, **2**, 410.

[63] *J.*, 1916, 370.

[64] *J.*, 1920, 378A.

[65] *J. Ind. Eng. Chem.*, 1921, **13**, 125 ; *J.*, 1921, 228A.

comprises those inorganic and organic bases which are believed to require the addition of hydrogen sulphide before they can form polysulphides; whilst the second includes thioureas, dithiocarbamates, thiourams, marcaptans, and disulphides, which either form polysulphides directly or break down into compounds capable of so doing. As examples of the first class, aldehyde-ammonia and *p*-phenylenediamine are cited, and as both of these substances evolve hydrogen sulphide when heated with sulphur at vulcanising temperature, their efficiency as accelerators should not be dependent upon the presence of either proteins or resins in the rubber. Hexamethylenetetramine is especially interesting as a compound belonging to both classes. During vulcanisation there are produced, amongst other products, both ammonia and carbon bisulphide, which alone or with basic products present in the rubber will form dithiocarbamates. Simultaneously with these, hydrogen sulphide is liberated, which, with the ammonia and sulphur, will produce polysulphides. In dealing with the inorganic accelerators, Scott and Bedford distinguish three types. Whilst the sulphides and hydrosulphides of the alkali metals are considered to belong to the first class, and accordingly are described as "primary accelerators," the action of litharge and zinc oxide is attributed merely to decomposition of the polysulphides by the removal of hydrogen sulphide, facilitating the removal of the sulphur; these compounds therefore being termed "secondary accelerators." The hydroxides and oxides of the alkali and alkaline-earth metals form an intermediate class, functioning initially as secondary accelerators during their conversion into the corresponding sulphides, which then take up sulphur and act as primary accelerators.

Some evidence in support of the correctness of these views regarding the behaviour of inorganic accelerators has been supplied by D. F. Twiss,[66] who has shown that the conversion of potassium hydroxide into the hydrosulphide does not affect its activity as an accelerator; they would be still further strengthened if lead sulphide were proved to be inactive.

The explanation of the action of the second class of accelerators is not, however, so straightforward.

The use of the thiourea and dithiocarbamate derivatives of organic bases, such as dimethylamine and piperidine, was suggested first by the Bayer Company in 1913,[67] the object being to provide a convenient means of introducing liquid or volatile bases into mixings in a solid, non-volatile form, which subsequently was assumed to decompose during vulcanisation with the liberation of the base. At this date, the action of accelerators was supposed to depend upon basicity alone, as is shown by the Bayer general

[66] *J.*, 1921, 247T.

[67] E.P. 11,615 and 12,777.

patent taken out in 1914, protecting the use of all bases having a dissociation constant higher than 1×10^{-8} [68].

Technical use soon brought to light the fact that the activity of the dithiocarbamate class of accelerator was greatly increased by the presence of a small proportion of zinc oxide in the mixing, the action of which had to be explained. Recently, G. D. Kratz, A. H. Flower, and B. J. Shapiro have suggested [69] that in the case of diphenylthiourea, an acid substance, probably a thiocarbamic acid capable of reacting with zinc oxide, is formed as one of the decomposition products, and that this zinc salt is the accelerator. Scott and Bedford, who appear initially to have considered that the activity of this class of accelerators depended on the presence or formation of the carbosulphydryl group, : C.SH, and that this, by the addition of sulphur functioned as a polysulphide, were subsequently led to modify their views, and in a paper by the latter and L. B. Sebrell,[70] it is suggested that the mechanism of the action of these accelerators can be explained by the formation of very active zinc salts.

The same conclusion has been reached independently by G. Bruni and E. Romani,[71] whose investigations appear to have been based on an observation made in 1917 by Ostromyslenski that zinc ethylxanthate is a very active accelerator. From the analogy between the xanthates and the dithiocarbamates, RO.CS.SM, $R_2N.CS.SM$, it seemed probable that the metallic derivatives of the latter would possess similar properties, and such indeed was found to be the case. These compounds, however, are not considered by Bruni to be the actual catalysts.

It has been shown by E. Romani [72] and by Scott and Bedford [73] that the thiouram disulphides are very powerful accelerators, and, according to the former worker, are themselves capable of effecting vulcanisation without the presence of additional sulphur.

The activity of the zinc alkyl dithiocarbamates and the corresponding xanthates has therefore been attributed by Bruni and Romani, and, independently, by A. Maximoff,[74] to a reaction taking place with the sulphur, resulting in the formation of zinc sulphide and a disulphide :—

$$(R_2N.CS.S)_2Zn + S \rightarrow ZnS + R_2N.CS.S.S.CS.NR_2.$$

In the case of the thiourea compounds, the formation of a mustard oil is assumed to take place first, monophenylthiourea giving

[68] E.P. 12,661.

[69] *J. Ind. Eng. Chem.*, 1921, **13**, 128 ; *J.*, 1921, 229A.

[70] *Chem. and Met. Eng.*, 1921, **24**, 835.

[71] *India Rubber J.*, 1921, **62**, 66 ; *J.*, 1921, 553A.

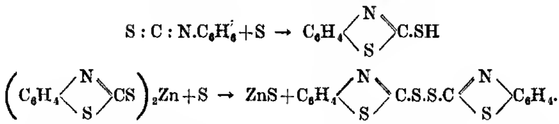
[72] *Giorn. Chim. Ind. Appl.*, 1921, **3**, 197 ; *J.*, 1921, 520A.

[73] *J. Ind. Eng. Chem.*, 1921, **13**, 125; *J.*, 1921, 228A.

[74] *Caoutchouc et Guttapercha*, 1921, **18**, 10,944, 10,986 ; *J.*, 1921, 668A.

phenyl isothiocyanate. This then reacts with sulphur, forming mercaptobenzothiazole, the zinc salt of the latter yielding a disulphide :—

$$C_6H_5.NH.CS.NH_2 \rightarrow S:C:N.C_6H_5+NH_3$$



In support of this theory, Bruni and Romani have prepared a series of mercaptothiazoles. These compounds were found to be inactive, but they become accelerators when converted into their zinc, lead, or mercury salts. The intermediate formation of a mustard oil during vulcanisation seems to be supported by the observation that, whilst tri-substituted thioureas act as accelerators, the tetra-substituted compounds which are not capable of this reaction are found to be inactive. D. F. Twiss, moreover,[75] has shown that phenyl isothiocyanate, in the presence of zinc oxide, is an accelerator, although not to the degree which might be expected.

According to Bruni, therefore, the activity of the carbo-sulphuryl group of accelerators is due to the formation of disulphide compounds —termed by him ultra-accelerators—which, by conversion into monosulphides, supply the sulphur in an active form for vulcanisation [76] :—

$$:C.S.S.C: \rightarrow :C.S.C: + S$$

Bedford and Sebrell, however, as a result of a study of the action of this class of compounds on the gel formation of rubber solutions in the cold, maintain the view that the effects are to be attributed to the formation of polysulphide derivatives of the metallic salts of the mercaptans, xanthates, etc., and not to the decomposition of these salts into the disulphides.[77] Whilst both these theories explain the need for the use of zinc oxide in conjunction with many accelerators, the results of further investigations must be awaited before the nature of the catalyst proper can be decided.

It should be noted also that, so far, no serious attempt has been made to explain the accelerative action of the nitroso compounds, although suggestions have appeared attributing this effect to the liberation of both hydrogen sulphide and sulphur dioxide during vulcanisation,[78] or to some action of the NO group on the double bonds of the rubber hydrocarbon.[79]

[75] *J.*, 1921, 247T.

[76] *Giorn. Chim. Ind. Appl.*, 1921, **3**, 196.

[77] *J. Ind. Eng. Chem.*, 1921, **13**, 1034 ; *J.*, 1922, 110A.

[78] Scott and Bedford, *J. Ind. Eng. Chem.*, 1921, **13**, 126.

[79] A. Angeli, *India Rubber J.*, 1921, **62**, 65.

Reference may now be made to the well-known fact that when organic accelerators are employed the extent to which combination has taken place between sulphur and rubber is no longer an index to the degree of vulcanisation as judged by physical and ageing tests.[80]

Some further investigations on this subject have been published by G. D. Kratz, A. H. Flower, and B. J. Shapiro,[81] which illustrate the remarkable development in the tensile strength of mixings containing zinc oxide and thiocarbanilide during the early stages of vulcanisation when the sulphur coefficient is still low. D. F. Twiss[82] incidentally brings out the same fact in a paper giving the results of further work on certain abnormalities shown in the stress-strain characteristics when hexamethylenetetramine is used as accelerator. It is proved that the temporary reversal of vulcanisation shown by this accelerator in the presence of zinc oxide disappears if the amount of the latter is increased over 2%, whilst it becomes more marked with reduced proportions of sulphur. This effect, which appears to be a special characteristic of hexamine, requires the presence of some finely-divided filler, such as carbon-black or zinc oxide, to develop, and is attributed to the formation during vulcanisation of some acidic decomposition product, which becomes masked by the presence of larger quantities of zinc oxide.

The mixings generally employed for experimental work are usually of the type: rubber 90, sulphur 10; which, although satisfactory for the purpose, are open to the objection that the proportion of sulphur is considerably higher than that normally employed in works practice, particularly in mixings in which accelerators are included.

For this reason, P. Schidrowitz and J. R. Burnand[83] have examined the behaviour of mixings containing approximately 4% and 2% of sulphur in the presence of piperidine piperidyldithiocarbamate and zinc oxide, and have studied the effect of the accelerator on the physical properties. Their results indicate that the addition affects the type or slope to a marked degree, and have led the authors to modify somewhat their views regarding the constancy of this characteristic.[84] It was found that the "toughness" is considerably increased, since at "technically correct" cures the stress at breaking point is increased by about 60% compared with the unaccelerated mixing, whilst the strain remains comparatively unaffected. It was, moreover, shown as a result of the examination of a series of mixings containing 2% of sulphur

[80] *Ann. Repts.*, 1920, **5**, 340.
[81] *J. Ind. Eng. Chem.*, 1921, **13**, 128; *J.*, 1921, 229A.
[82] *J.*, 1921, 242T.
[83] *J.*, 1921, 268T.
[84] *Ann. Repts.*, 1919, **4**, 334; 1920, **5**, 346.

and 2½% of zinc oxide, that for satisfactory results the proportion of the accelerator should not fall below a critical value lying between 0·25% and 0·50%.

An examination of the efficiency of various organic and inorganic accelerators in a zinc oxide mixing has been made by H. A. Endres,[85] whilst the results of experiments on similar lines with a series of lead compounds have been published by J. M. Grove.[86]

In conclusion, attention might be drawn to the suggestion put forward by J. B. Tuttle,[87] that the variability of plantation rubber should be tested in a mixing containing a small proportion of zinc oxide, on the ground that a better indication of the behaviour of the material under technical conditions should be obtained as a result of the removal of any acidic substances giving full scope to the natural accelerators present. The adoption of this proposal, however, would probably tend to reduce rather than accentuate the variability shown by tests in simple rubber-sulphur mixings, and thereby diminish the incentive for the production of a uniform product suitable for all classes of rubber manufacture.

Compounding Ingredients.

There is comparatively little to record in connexion with compounding ingredients, the importance of fineness of division, referred to in previous reports, being now fully appreciated. For this reason the properties of clays, either natural such as "Bentonite," or specially prepared in a fine state of division,[88] are receiving considerable attention, and these have been suggested[89] as a suitable medium for the introduction into mixings of the more active accelerators. In connexion with the difficulties incidental to the introduction of carbon-black into mixings, it has been suggested that the evolution of dust could be avoided, and more uniform mixing secured, by first incorporating the pigment in a solution of glue,[90] a material which, incidentally, appears to have enjoyed considerable popularity with American manufacturers as a compounding ingredient.

Passing reference might be made, in connexion with the compounding of rubber, to the recent development of various types of automatic mixers, in which the operation is carried out in an enclosed chamber.

[85] *Caoutchouc et Guttapercha*, 1921, **18**, 11,089; *J.*, 1921, 858A.

[86] *India Rubber World*, 1921, **64**, 663; *J.*, 1921, 668A.

[87] *J Ind. Eng. Chem.*, 1921, **13**, 519; *J.*, 1921, 709A.

[88] Schidrowitz, W. Feldenheimer, and W. W. Plowman; E.P. 153,343; *J.*, 1921, 19A.

[89] P. Schidrowitz, and Catalpo, Ltd., E.P. 170,682; *J.*, 1921, 898A.

[90] Goodyear Tire and Rubber Co., E.P. 146,993 and 161,483; *J.*, 1921, 400A.

The Stress-Strain Curve.

The subject of the interpretation of the results of the stress-strain curve has been dealt with in considerable detail in preceding reports,[91] particularly in respect to the theory of Schidrowitz and Goldsbrough, that the "type" or "slope" represented by the inclination of the latter part of the curve to the stress axis is for any one mixing independent of the degree of vulcanisation. This conclusion has been contested by various workers, including O. de Vries and, more recently, H. P. Stevens.[92] The former has stated that the inclination increases with progressive vulcanisation,[93] whilst the latter observer finds the reverse effect to obtain.

In discussing these discrepancies, P. Schidrowitz[94] puts forward the suggestion that thermal effects may have some influence on the results, since the rates of loading employed by de Vries and Stevens were much higher than those used in his original investigation.

Reference has already been made to the effect produced on the slope of the stress-strain curves by the addition of accelerators to mixings; it being shown by Schidrowitz and Burnand[95] that in such cases, not only is the slope variable, but in place of the average figure of 35 units for a standard rubber-sulphur mixing, results of 28 and 29 are frequently obtained, illustrating the fact that by the use of appropriate accelerators special physical properties may be imparted to the rubber.

In a recent paper, E. Hatschek[96] suggests that, in place of the customary representation of "elongation" against the load, calculated on the original cross-sectional area, which takes no account of the changes resulting from stretching, a more rational and simple method would be to plot the strain against the stress calculated on the corresponding cross-sectional area. The same proposal has been put forward by J. W. Shields.[97] This modification is rendered possible by the fact that the volume of rubber in a pure mixing may be taken to remain constant within wide limits during deformation. If, however, fillers are introduced, it has been shown by H. F. Schippel[98] that this assumption is no longer justifiable.

When the results are plotted in this way, the inflexion which is normally shown at an elongation of 100% disappears, and the

[91] See *Ann. Repts.*, 1919, **4**, 334; 1920, **5**, 346.
[92] *Bull. R.G.A.*, 1921, **3**, 246; **5**, 1922, 67A.
[93] *J.*, 1920, 308T.
[94] *India Rubber J.*, 1921, **62**, 481.
[95] *J.*, 1921, 268T.
[96] *J.*, 1921, 251T.
[97] *India Rubber J.*, 1921, **62**, 692.
[98] *J. Ind. Eng. Chem.*, 1920, **12**, 33.

change in curvature and slope becomes quite gradual.[99] The nature of the curves thus obtained has been examined and found to be representable by the equation for a rectangular hyperbola. Such being the case, if *a* be the distance of the asymptote from the axis of the curve, and *b* the intercept cut off on the asymptote by the tangent to the curve at the axis, it follows that the product *ab* will determine the size or scale of the hyperbola, whilst the relative values of *a* and *b* will determine the proportion of the curve lying above the stress axis. It is suggested by Hatschek that further investigation may show the product *ab* to be a characteristic of the rubber, and the corresponding ratio to depend on the degree of vulcanisation.

Whilst this method of representation is very interesting for the purpose of comparing the properties of rubber with those of other more rigid materials which follow Hooke's law, there is much to be said for the view expressed by P. Schidrowitz[100] that, by so doing, one of the important characteristics of the material is masked, and that, by eliminating the sharp inflection point shown by the curve as normally plotted, a property of technical importance becomes obscured.

A further point of some interest is evident when examining the curves obtained with the Schopper ring-testing machine—namely, the existence of a brief period near the origin during which, contrary to what might be expected, the application of stress produces comparatively little change in the strain. This may be due to deformation taking place in the test pieces, as suggested by Hatschek (*ibid.*), but the same effect is shown to a marked degree by crude rubber which has become somewhat hard as a result of keeping.

Physical Properties.

The important work of W. B. Wiegand on the stress-strain characteristics of rubber[101] has been continued, and a further paper contains the results of an investigation into the energy transformations which occur during stretching.[102] It is pointed out that the work applied in deforming the material is transformed into three forms, viz., stored potential energy, reversible heat, and frictional heat, and on rapid retraction the potential energy is largely retransformed into work, whilst a further development of frictional heat occurs. The form of the hysteresis cycle, therefore, will obviously depend on whether the tests are carried out rapidly or slowly to facilitate the dissipation of the energy transformed into heat, the latter being the method which Wiegand found the more satisfactory.

[99] *India-Rubber J.*, 1921, **62**, 959.

[100] *India-Rubber J.*, 1921, **62**, 679.

[101] *Ann. Repts.*, 1920, **5**, 343.

[102] *J. Ind. Eng. Chem.*, 1921, **13**, 118; *India-Rubber J.*, 1921, **61**, 663; *J.*, 1921, 229A.

The preliminary results showed that the energy losses due to heat development became very marked for elongations exceeding 300%, the curve obtained by plotting elongations against hysteresis loss being a rectangular hyperbola. Consequently, for the subsequent experiments to determine the effect of the degree of vulcanisation and the addition of fillers, an extension of 200% was employed, with a rate of extension in the neighbourhood of 20 inches per minute. In this way it was found that the energy loss due to the development of frictional heat amounted in the case of a pure mixing to only 4% of the total work, and that this figure further slightly diminished by over-vulcanisation. When, however, 5 and 20 volumes of zinc oxide are introduced into the mixing, the losses are increased to 8% and 14%, respectively. Against this increased heat development shown by compounded mixings under stress, however, has to be set the improvement effected in the thermal conducticity,[103] in which respect zinc oxide would seem at first sight to possess considerable advantages over carbon black. With a pneumatic tyre, however, the transformation of energy into heat in the rubber tread is small in comparison with that taking place in the cotton fabric or cords of the casing, and Wiegand gives some interesting results showing the relation between the number of plies of canvas and the energy consumption on flexion as shown by pendulum measurements.

The subject dealt with by Wiegand in the present and previous papers is one of great technical importance, and his work should serve as a stimulus to further research in connexion with the various factors which determine the efficiency and durability of motor tyres.

The well-known "grain" sometimes shown by articles made from calendered sheet has been investigated by A. van Rossem,[104] who shows that the property—consisting of a marked difference in the stress-strain characteristics between the transverse and longitudinal directions—disappears when the material is heated to 70° C. for two hours and allowed to shrink freely.

It has been suggested by R. W. Lunn[105] that this effect may be explained by assuming spheroidal particles of a viscous liquid enveloped by an elastic skin, which are flattened and elongated in one direction by passing between the rolls of the calender. It is assumed that, whilst the viscosity of the internal liquid is sufficiently high at ordinary temperatures to maintain the particles in a deformed condition, this becomes reduced on warming, with the result that recovery can then take place.

The observation by W. B. Wiegand,[106] that treatment with a

[103] A. A. Somerville, *India-Rubber J.*, 1921, **62**, 89, 94.
[104] *India-Rubber J.*, 1921, **62**, 343 ; *J.*, 1921, 667A.
[105] *India-Rubber J.*, 1921, **62**, 831.
[106] *India-Rubber J.*, 1921, **62**, 733.

solvent is equally effective in removing "grain" appears to show that this phenomenon is not a "Joule" effect, as supposed by van Rossem, but is in some way connected with viscosity, as suggested by Lunn.

The solubility of various organic compounds in rubber has been investigated by G. Bruni, employing the "cooling curve" method[107]; the results with naphthalene, azobenzene, etc. show rubber to behave as a normal solvent; whilst H. P. Stevens, in his work on the vulcanisation of rubber in solution, has produced further evidence in support of the greater solubility of sulphur in vulcanised, compared with raw, rubber.

Some experiments on absorption of light by caoutchouc in ethereal solutions have been carried out by S. J. Lewis and B. D. Porritt,[108] whose results indicate that this is of the general type, and not pronounced for wave lengths greater than 2700 units. Whilst this explains the protective influence exerted by certain dyes against the detrimental effects of sunlight,[109] the work has not been carried far enough to afford any evidence regarding the constitution of rubber. The suitability of rubber sponge as an insulator for cold storage chambers has also been examined.[110] When specially prepared in a highly cellular form, this material was found to possess a heat conductivity lower than that of any of the numerous other insulators investigated, and, if it could be produced commercially in suitable form, a new application for rubber would appear to be in prospect.

Ageing.

The need for some quick test to indicate the durability of rubber goods has been felt by the manufacturers from the earliest days of the industry, but, so far, no thoroughly reliable method has been devised for the purpose, probably for the reason that the changes which occur are undoubtedly complex and influenced by different factors according to circumstances. This fact is emphasised by O. de Vries and H. J. Hellendoorn,[111] in a paper giving the results of ageing tests on a series of cures of a 92·5 : 7·5 rubber-sulphur mixing over a period of two years. The results of the physical tests on these samples show that whilst the strain steadily diminishes, the stress initially increases on keeping, but later diminishes.

Whilst this behaviour is in general agreement with the work of Stevens and other investigators, the fact that the results do not show any marked signs of instability in the case of over-vulcanised

[107] *Rubber Age*, 1921, **2**, 280.

[108] *J.*, 1921, 18T.

[109] B. D. Porritt, *India-Rubber J.*, 1920, **60**, 1159 ; *J.*, 1921, 19A.

[110] *Food Investigation Board, Special Report No.* 5, p. 55 ; H. M. Stationery Office, 1921.

[111] *India-Rubber J.*, 1921, **61**, 87.

samples containing between 4% and 6% of combined sulphur must be surprising to those familiar with technical conditions. It has, however, been suggested[112] that these abnormal results may be due to the special climatic conditions under which the tests were carried out, the presence of considerable quantities of water vapour having been found to exert a protective influence.[113]

In carrying out ageing tests, in addition to considering the effects produced by light, temperature, and water vapour, attention should be paid to the well-known fact that all rubber goods tend to become hard on prolonged storage, and require warming or mechanical treatment to produce a flexible condition in which any permanent alteration in physical condition can be detected.[114] Having regard to the variety of factors which influence the ageing of rubber, it is not surprising to find W. C. Geer and W. W. Evans[115] emphasising the need for caution in interpreting the results obtained by accelerated tests carried out in hot-air ovens at 160° F. These workers find that under these conditions a period of three or four days is generally sufficient to yield useful information regarding the durability of a sample, particularly in respect to the effect of over-vulcanisation.

The statement, referred to in last year's report,[116] that the substitution of carbon-black for zinc-oxide produces an adverse effect on the ageing qualities of a mixing, has been subjected to severe criticism by W. B. Wiegand,[117] and, in the light of long technical experience since the days of Hancock, there seems little reason to anticipate any detrimental effect resulting from the use of this pigment, provided it be satisfactory in quality.

Miscellaneous.

A welcome feature of the year has been the material development of a wider interest in the underlying problems of tyre manufacture and usage, which formed the subject of a paper read by C. Macbeth[118] before the Institution of Automobile Engineers.

As progress in tyre design obviously must involve the study of conditions of usage as well as methods of manufacture, the proposed initiation of an investigation into the complex problems of car suspensions by the British Motor Research Association is a development of considerable importance to the rubber manufacturer.

Another important problem common to the rubber and motor industries is that presented by the supply of petrol and similar

[112] H. P. Stevens, *India-Rubber J.*, 1921, **61**, 310.
[113] *Ann. Repts.*, 1920, **5**, 345.
[114] P. Schidrowitz, *India-Rubber J.*, 1921, **61**, 261.
[115] *India-Rubber J.*, 1921, **61**, 1163.
[116] *Ann. Repts.*, 1920, **5**, 346.
[117] *India-Rubber J.*, 1921, **61**, 604.
[118] *India-Rubber J.*, 1921, **61**, 929, 975, 1021, 1071.

solvents, which have greatly increased in price during recent years. For this reason, processes designed for the efficient and economical recovery of solvents are now of considerable interest, and attention may therefore be directed to two recent papers, by I. Masson and T. L. McEwan,[119] and A. A. Drummond,[120] dealing with cordite solvents, as well as to the promised publication by the Department of Scientific and Industrial Research of fuller details regarding the plant and working of solvent recovery installations in Government factories during the war.

As the methods hitherto used or suggested for the separation of solvent vapour from air have, in general, depended upon either direct condensation by cooling or absorption in some high-boiling liquid, a recent proposal to employ silica gels for this purpose should not be overlooked.[121]

Analysis and Testing.

It is to be regretted that for the time being the subject of rubber analysis does not appear to be receiving the attention which its importance and imperfections deserve.

During recent years consideration appears to have been directed more to physical than to chemical methods, and, as an example, the suggestion that X-ray examinations might prove of technical value[122] has been taken up and successfully employed for the testing of golf balls.

The importance now attached to the fineness of division of compounding ingredients has naturally brought the microscope into prominence as a means of determining not only the average particle size of fillers, but the uniformity of their dispersion in the rubber mixing. The difficulty which has stood in the way of the general application of microscopical methods to the examination of rubber has been one of technique, it being impossible to prepare satisfactory specimens for the purpose by the usual wax embedding method, except with material in which a film of rubber is firmly anchored by textile fibres. By the use of the freezing method, however, H. A Depew and I. R. Ruby[123] have succeeded, by employing liquid carbon dioxide supplemented by liquid air, in preparing sections sufficiently thin for examination by transmitted light, and as an alternative it has been suggested that the necessary rigidity for cutting might be obtained by treatment with dilute

[119] *J.*, 1921, 32T.

[120] *J.*, 1921, 284T.

[121] E. B. Miller, *Chem. and Met. Eng.*, 1920, **23**, 1155, 1219, 1251; *J.*, 1921, 109A.

[122] *Nature*, 1920, **104**, 698.

[123] *J. Ind. Eng. Chem.*, 1920, **12**, 1156; *India-Rubber J.*, 1921, **61**, 37; *J.*, 1921, 52A.

sulphur chloride solution.[124] The methods outlined seem likely to remove the difficulties experienced in the past, and before long microscopical examination may be included amongst the standard tests to which rubber samples are subjected.

The determination of hardness has been a test upon which much thought and ingenuity have been expended, particularly in connexion with the products of metallurgical industries. In the case of rubber goods, the wide variation in the physical properties due to differences in the degree of vulcanisation and the proportion of compounding ingredients has rendered the problem one of special difficulty. For this reason a paper by H. P. Gurney,[125] dealing with this question, is worthy of careful attention, although it can scarcely be expected that any one instrument will be found applicable to materials so diverse in character as masticated rubber and ebonite.

The examination of balloon fabrics has formed the subject of two publications during the year, by A. W. Ritchie[126] and J. W. W. Dyer.[127] Although these papers are of considerable interest to those concerned with the manufacture of such materials, the methods of testing described are not particularly novel, being largely based upon those evolved by the National Physical Laboratory and earlier workers on this subject.

From the analytical standpoint, the two most interesting communications which have appeared deal respectively with the detection of accelerators in vulcanised samples and the examination of antimony sulphide.

As a result of a study of the former problem, D. F. Twiss and G. Martin[128] find that the presence of organic accelerators in a mixing results in an increase in the nitrogen content of the acetone-soluble constituents of the vulcanised material. The mean value for material made up from *Hevea* plantation rubber has been found to be approximately 0·03%, calculated upon the original weight of the rubber, and if a figure is obtained exceeding 0.05% the use of an organic accelerator containing nitrogen may be suspected, particularly if the relationship between the physical characteristics and the coefficient of vulcanisation proves to be abnormal. The identification of the particular accelerator used is evidently a much more difficult matter, since, during the process of vulcanisation, these substances, which are used in small proportions only, become largely transformed into other products. A general scheme of

[124] H. Green, *India-Rubber J.*, 1921, **62**, 622.

[125] *J. Ind. Eng. Chem.*, 1921, **13**, 707; *India-Rubber J.*, 1921, **62**, 497; *J.*, 1921, 819A.

[126] *Advisory Committee for Aeronautics, Report and Memoranda, Nos.* 360, 584, 614; H.M. Stationery Office, 1921.

[127] *Aeronautical J.*, 1921, **25**, 332.

[128] *India-Rubber J.*, 1921, **61**, 1283; *J*, 1921, 520A.

analysis has been suggested, involving the examination of the extracts obtained by treatment with acetone, water, and hydrochloric acid respectively, by which it is claimed an indication as to the type of accelerator present can often be secured. Further work would appear necessary on the behaviour of various accelerators in different types of mixings, both pure and compounded, before the formulation of a reasonably general method of detection can be expected.

In contrast to the foregoing problem, the analysis of antimony sulphide is a subject which has attracted attention for many years, the question usually at issue being whether the free sulphur extracted by treatment with boiling carbon bisulphide is an accurate index of the amount present under the conditions of vulcanisation. The results of an investigation into this matter have been published by B. D. W. Luff and B. D. Porritt,[129] who show that the higher sulphide suffers appreciable decomposition at 140° C., with the liberation of additional sulphur, and direct attention also to the possibility of insoluble sulphur ($S\mu$) being present in samples of the pigment. For these reasons it is suggested that samples should be heated to 150° C. for five hours in an alkaline atmosphere before extraction, in order to decompose the higher sulphide and to convert any insoluble sulphur present into the soluble form. It is proposed that the result of this determination should be described as "available sulphur," a term independently suggested by D. F Twiss.[130]

From this work it would seem that the higher sulphide of antimony is not decomposed by low-boiling solvents, as has been assumed by many previous investigators, and that no appreciable decomposition takes place until a temperature in the neighbourhood of 130° C. is reached, when the red trisulphide is formed with the liberation of sulphur.

Whilst the stability of the higher sulphide, which has recently been stated to be a tetra- and not a penta-compound,[131] may be regarded as satisfactorily settled, there is still room for further work to explain the somewhat surprising fixation of sulphur noticed by Luff and Porritt in the case of certain samples heated at 120° C.

[129] *J.*, 1921, 275T.

[130] *India-Rubber J.*, 1920, **60**, 1014; *J.*, 1922, 20T.

[131] F. Kirchhof, *Z anorg. Chem.*, 1920, **112**, 67; *J.*, 1920, 721A.

LEATHER AND GLUE.

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The year 1921 will long be remembered in the annals of the leather trade as one of the most abnormal periods in the history of the industry. It cannot be said to have been the worst year the trade has experienced, because many firms have had no short time, but on the other hand some have been shut down during the greater part of the year. The tanners and manufacturers who have managed to dispose of their output have been those enterprising people who could adapt themselves and their production to the abnormal demands which arose. This has applied more particularly to the light leather manufacturers.

Two factors have greatly influenced the leather trade during the past twelve months, *viz.*, the price of raw hides and the price of raw calfskins. A great slump in trade set in towards the middle of 1920. In some districts and in the case of sole leather generally, the demands fell off after Easter, 1920, and consequently the sole leather tanners were obliged to reduce their input of raw material. The price of raw hides still remained at its high level, partly owing to the much higher cost of imported raw skins. It seemed evident to the tanners that no progress could be made until the price of hides had been reduced to a more reasonable level. With this object in view the United Tanners' Federation decided that in view of the slump some attempt should be made to cope with the abnormal situation which had arisen, and the members pledged themselves to reduce their input of raw material by 50%. The inevitable drop in the price of the raw material was effected, and the price of raw hides fell to below 5d. per lb., a figure which had not been known for nearly 20 years. This was the price ruling about Easter, 1921, and it became quite a tempting figure for the tanner. He commenced to lay in stocks at this figure, with the result that prices commenced to firm up, and there was a gradual increase from 5d. to 11d. in October. It is probable that the price of hides will stabilise around this figure, which is about 50% above pre-war costs. The heavy leather trade was in a very depressed condition at the beginning of the year. Stocks were being realised at most ridiculous figures, but having disposed

of their high-priced stocks, tanners developed confidence, and the year has closed with a certain amount of misgiving as to the volume of future trade, but with a firm assurance that there will be sufficient home trade to maintain a restricted economic production until the export trade revives.

The position in the upper leather trade is rather different. Sole leather tanners have had nothing to fear from foreign competition because the adverse exchange rates tended to exclude American imports, but the greatest competitors in calf leathers are the French and German manufacturers, who were considerably aided by the exchange rates. Raw calfskins had slumped in price early in 1920, but very few English tanners had taken advantage of this low figure, with the result that the price slumped still further to 8d. per lb., which, with manufacturing expenses, labour and overhead charges at 7d., enabled box-calf to be produced at a small profit at 1s. 6d. per foot. French calf was being imported in small quantities in 1920, but owing to its vastly superior quality and the large demand it was realising very high figures. When the winter slump reached its worst the price of imported calf slumped also and French calf was procurable at 2s. per foot. The German manufacturers had now begun to export to this country, and the low price of the mark enabled them to cut the figure to 1s. 6d. and later to 1s. 3d. per foot, at which price it was impossible for English or French manufacturers to compete. The English tanners were thus compelled either to shut down or to seek to improve their productions and surpass the imported German leathers. Many firms in the North elected to close down and have not opened since, but the manufacturers in the Midlands and in Scotland have exhibited more enterprise. They have made strenuous efforts to compete with the German and French tanners as regards quality, and in the opinion of some of the leading boot manufacturers—and they are keen critics—some of the upper leather produced in the British Isles to-day is equal, if not superior, to the best German and French productions. Some of the willow calf being dyed and finished in the Midlands approaches as near perfection as we can ever hope to finish a natural and variable product such as hides and skins.

As regards the production of glazed kid, great strides have been made in this direction by many young firms. Some of the black glazed kid manufactured by young and progressive tanners is openly acknowledged by the boot manufacturers to be quite equal to the best American productions—which is a great admission on their part. But the Americans still maintain a splendid supremacy in dyeing and finishing coloured glazed kid, and there seems no likelihood of that supremacy being challenged. Leather dyeing is one of the weakest links in the British leather industry, and no

work has been published during the past few years which shows any signs of progress. There is still a close veil of secrecy maintained in respect of leather dyeing, but progress is being made in certain directions, as evidenced by the excellent willow calf which is being obtained. As yet, however, this progress has not extended to glazed kid.

This year has witnessed a further growth of the leather and glue industries in our colonies, and some of them are beginning to export high-class leathers to the home country. Canada, Australia, India, and South Africa have all shared in this development. The universal slump in trade has caused a temporary lull in some colonies, but it is only temporary, and the home tanners are already looking to their laurels. The leather trade in other countries has been passing through very critical times—America, Germany, and France are the only ones which need be mentioned. The slump has been a very serious blow to the American leather trade, but it has weathered the storm. The French and German tanners have not been so badly hit by the slump as by the shortage of materials. Germany, in particular, has passed through some very strange experiences. Her leather factories have not been able to work at their maximum output owing to difficulties in securing raw materials. It is not very clear why, but it appears as if the financial straits of that country are the root cause.

In general, the position is very encouraging, and particularly for the British leather industries. Many tanners are manifesting a keen enthusiasm for improvement; the standard of British production all round is being raised. The business heads are keenly alive to the need for new blood and new methods, whilst retaining all that is best in the old. A revolution has been brought about in liming processes which would have been deemed impossible in pre-war days. Deliming and bating are likewise being modified in accordance with the latest researches on the subject. The British tanners are becoming more and more imbued with scientific ideas, and they are beginning to realise the necessity for close chemical control of all purchased chrome tanning liquors or, what is much better, they are manufacturing their own tanning liquors. Fat liquoring is still not very clearly understood, and the tanners of to-day prefer bought mixtures to pure products, which they can mix to suit their own requirements. There is considerable scope for the application of the principles of hygrometry to the drying plants in many leather factories. The latest type of machine is built up on very sound scientific principles. The finishing of heavy, light, and dressing leathers has long been a foreman's secret handed on carefully to sons and friends, but serious inroads are being made into the unexplored realm of that knowledge. The application of pigment finishes, which was referred to last year,

has been considerably extended. An English company has been formed to manufacture the finishes in this country, and strenuous endeavours have been made to familiarise tanners and dressers throughout the kingdom with their properties and application. The German practice of lightly buffing the grain of all heavier skins is being generally adopted and a superior finish and appearance is being obtained.

Leather manufacturers throughout the country have begun to realise the truth of the late Lord Allerton's dictum: "Leather is made or marred in the limeyard." The liming process has been revolutionised in many factories.

It is very gratifying to find that the thirst for knowledge continues. The Leeds University Leather Industries Department[1] has been enlarged during the last year, to provide laboratory accommodation for additional students. More convenient quarters have been provided for the study of bacteriological and microscopical problems in connexion with the industry. The entry of students has constituted a record in the history of the department and applications from abroad have been refused owing to the unprecedented numbers of British and Colonial applicants. A large amount of valuable research work has been carried through at this institution and it is exerting a very beneficial influence on the trade.

The Leathersellers' Company's Technical College has had one of its most successful sessions since the inception of the college; 60 students have been in attendance during the year and a very high standard of proficiency has been reached, as evidenced by their success in public examinations. The Northampton Technical School Leather Department has had a most successful session and the entries for full-time day courses for the new session have taxed the accommodation of the department to its limit. The students at the Runcorn Technical School have distinguished themselves, and the Leather Section there has had a very useful session. The growth of educational facilities and the active interest manifested by members of the trade in the different centres where these institutions are situated, are significant features of the general trend of the trade. The manufacturers are keenly alive—as they have never been before—to the importance of science to their trade. They are acting on advisory committees in connexion with these educational institutions and affording many facilities to their employees to participate in the training.

A further gratifying feature of the year has been the pride exhibited by the leather manufacturers in their new Research Association, which has prosecuted its investigations during the year. Reports have been circulated to members, but the information

[1] *Leather Trades Rev.*, 1921. 329.

in them is confidential. Several new research stations[2] have been established in different parts of the world for investigating problems in leather manufacture. The American Tanners' Council has fixed upon the University of Cincinnati as the centre for a research laboratory and researches are being continued in colloid chemistry at the Columbia University as a result of an annual grant by a large firm of leather manufacturers in Milwaukee. A new research institute for the leather industry is to be erected at Dresden, Germany, towards the cost of which £400,000 has been contributed by the industry itself, £150,000 by the Export Bureau, and substantial amounts by the City of Dresden and the State of Saxony. It is also proposed to establish a research station and experimental plant in the United Provinces in India and a leather research institution is to be established in Sweden. The British Boot, Shoe and Allied Trades Research Association has done some valuable work during the year and has published a preliminary report on the properties desired in welted insole leathers.

For a long time it has been felt that there was a great dearth of up-to-date literature for the trade. The standard textbooks have been published over ten years and none of the authors has been able to devote time to the task of revising their publications. The most valuable textbooks are out of print, and it has become a matter of great concern to many that no fresh publications were being issued. The Germans have been far ahead of us in this respect, and the number and variety of their technical publications have been astounding. It is very gratifying to find some attempt made to remedy this lack, and the following books have appeared during this year: "Tanning Materials[3] (with notes on Extract Manufacture)," A. Harvey, Crosby, Lockwood and Son, London; "Animal Proteins,"[4] H. G. Bennett, Balliere, Tindall and Cox, London, and "Practical Leather Manufacture,"[5] H. G. Crockett, Leather Trades Publishing Co., Ltd. In addition to these new books in English, there has appeared a new journal for leather chemists, *Zeitschrift für Leder- und Gerberei-Chemie*, edited by Dr. Moeller, and published by Otto Meissner Verlag, Hamburg.

Soaking and Liming.

Hitherto very little attention has been paid to the raw skin. It has been generally recognised that its nature did influence the finished leather and that stale goods were inferior to fresh skins, but the tanner has not taken any special precautions to avoid

[2] *Ibid.*, 1921, 860.
[3] *Ibid.*, 1921, 476.
[4] *Ibid.*, 1921, 859.
[5] *Ibid.*, 1921, 884.

loss in raw goods. G. D. McLaughlin[6] has studied certain characteristics of fresh hide thirty minutes after it has been flayed. He observed that at concentrations greater than $N/20$, organic acids produced most swelling of the corium. Further swelling was caused by immersing the acid swollen pelt in lactic acid. Sodium, potassium, and ammonium chlorides exerted a swelling action on the corium, whilst the chlorides of the heavy metals possessed a small swelling power only, in some cases dehydrating the pelt. Less acid swelling was obtained if the pelt had been treated with metallic chlorides first. In later experiments[7] McLaughlin showed that the swelling properties of pelt were very adversely affected by allowing the freshly flayed skins to remain exposed to the air. The corium was swollen with lime water and the amount of swelling obtained diminished 25% by exposure to the ordinary atmosphere for 4½ hours. Acid was formed in the skin and the amount formed was determined by alkalimetric titration. Experiments are being continued to determine the effect of solutions of different salts on the hide.

H. C. Ross, H. C. Marris, and Wm. Walker and Sons, Ltd., have taken out a patent[8] which bears on this subject. They find that certain enzymes are present in the cells of the skin and these can start putrefaction. Thrombase is produced by the living cells composing the skin just before the cells die. Saprophytic bacterial infection produces a proteoclastic enzyme which exerts a detrimental action on the hide or skin. The patentees have proposed to preserve hides and skins from the action of the thrombase by treating them with ammonia or other end products of the action of that enzyme and from the action of the "saprophase" or proteoclastic enzyme by disinfection. A mixture of potassium oxalate, peptone, phenol, and glycerin is suggested in the specification. They ascribe the deterioration or partial depilation of skins after flaying to the action of these enzymes, particularly saproprotease and thrombase, and in a subsequent patent[9] propose to use this action for unhairing hides and skins. The hides are dipped in a weak solution of ammonia and calcium polysulphide or lactate. The ammonia inhibits the action of the bacterial enzymes but does not inactivate the physiological enzyme, thrombase, which is formed around the hair roots. The calcium polysulphide or lactate is added to activate the thrombase and, if thought necessary, a small addition of trypsin can be made to the unhairing liquor.

The British Leather Manufacturers Research Association has been occupied on the problem of the bacteria occurring in soaks.

[6] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 295; *J.*, 1921, 669A.

[7] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 435; *J.*, 1921, 781A.

[8] E.P. 169,468; *J.*, 1921, 820A.

[9] E.P. 169,730; *J.*, 1921, 820A.

They have isolated a tremendous number of organisms, and it is their intention to investigate the characteristics and effects of each individual organism. Some eminent leather trades' chemists hold the view that the soak liquors and the bacteria present in the waters used in different tanneries play a very important part in the quality of the leather produced. There are certain indications that enzymes have a very desirable action on the fibres, but further work is required on the subject.

The subject of bacteriology and microscopy has been very much to the front during the past twelve months in connexion with the leather trade. W. Moeller[10] has written a number of articles on the structure of the hide fibres. A. Seymour-Jones[11] has made a series of valuable contributions to our knowledge of the skin as it enters into the art of leather manufacture, and in conjunction with F. L. Seymour-Jones[12] has given a sketch of the applications of the microscope to the leather industry. The valuable researches carried out by A. Seymour-Jones and the most excellent account which he has published have stimulated the interest of many workers in this branch of the science.

A writer some years ago stated that the leather industry presented a very profitable field of research to the technical mycologist. One firm of consulting chemists has instituted a special branch for the express purpose of specialising on the technical mycology of the leather trade. This enterprising firm has commenced the publication of a bulletin containing a record of the most important work carried out by this branch, and the second issue[13] contained an account of an investigation of the causes of "run" pelts in the sweating process. This defect was traced to nematodes, organisms of a worm-like character which live on organic fluids. They belonged to the family *Nemathelminthes* and are found in all decaying vegetable and organic matter. They did not appear to be present in the skins on arrival at the tannery but were found in the sweating chamber itself, and it is suggested that they arise through insufficient regard for cleanliness in that chamber.

R. H. Marriott[14] has unhaired skins by the aid of dilute acids, particularly acetic acid, and he considers that this depilatory action is not bacterial but probably due to the hydrolytic action of the acid on some prosthetic protein similar to mucin, the carbohydrate group being attacked by some ferment which develops in the liquor. Acid unhairing is not so effective as ordinary liming as shown by the presence of the sudoriferous and sebaceous glands

[10] *Collegium*, 1916 and 1918.
[11] *J. Soc. Leather Trades Chem.*, 1918, **2**.
[12] *Ibid.*, 1921, **5**, 56.
[13] *Bulletin No. 2 of the Bureau of Bio-Technology, Leeds*; *J.*, 1921, 230A.
[14] *J. Soc. Leather Trades Chem.*, 1921, **5**, 2; *J.*, 1921, 230A.

in the unhaired skin. There is some bating action since a skin unhaired with acid, tanned, and finished without bating, was softer than a limed and bated skin, and Marriott[15] has repeated his experiments with both calf and goatskins and mounted sections for microscopical examination. A. Seymour-Jones[16] has applied trypsin in the form of a paste to the grain only of skins, previously delimed with acetic acid, and has shown that the elastic fibres are digested. J. T. Wood[17] has patented the application of an enzyme paste to the grain of skins for puering and bating. Several works are bating for very short periods of time and obtaining leather of excellent quality.

J. A. Wilson[18] has prepared photo-micrographs of sections of skin before and after bating with trypsin; these reveal an absence of elastic fibres after the bating process. He concludes that bating consists of the reduction of limed skins to a state of minimum swelling and the digestion of the elastin fibres present in the grain membrane. Marriott criticises this. He admits that elastin is digested by an enzyme bate but this digestion is not essential to the bating process, since he has obtained softer and better leathers by merely unhairing with ½% acetic acid solutions and not bating at all. He suggests that the solution of the cementing substance is one of the essential features of true bating. After discussing the lack of optical activity of elastin under polarised light, he concludes that the elastin fibre is either a liquid or a semi-solid like gelatin solution. The writer is acquainted with several prominent firms who omit the bating process entirely from their willow and box calf manufacture. The skins are delimed with acetic acid, then pickled and tanned.

W. Rautenstrauch[19] has patented the use of $N/10$ barium hydroxide solutions for unhairing. R. Hilgermann and M. Emmerich[20] prepare an enzyme mixture from cultures of *B. emycoides tumescens*, *megatherium*, and *mesentericus* and certain moulds, *Mucor* and *Aspergillus*. Hides are softened with acid and alkali, placed in water, and treated with the enzyme preparation for 24–96 hours at 22°–25° C. to loosen the hair. The Chicago Process Co.[21] has patented a process for liming and unhairing hides by giving one day in a used lime and sulphide liquor, then one day in a used lime liquor to which has been added about 2% of sodium sulphide on the weight of the hides. After one day in this liquor the hides are washed and passed through four lime liquors the last

[15] *Ibid.*, 1921, **5**, 280; *J.*, 1921, 781A.
[16] *Ibid.*, 1920, **4**, 291; *J.*, 1921, 123A.
[17] E.P. 154,103; *J.*, 1921, 53A.
[18] *J. Soc. Leather Trades Chem.*, 1921, **5**, 15.
[19] G.P. 304,251 and 338,095; *J.*, 1921, 442A, 632A.
[20] G.P. 334,526; *J.*, 1921, 442A.
[21] E.P. 163,109; *J.*, 1921, 480A.

of which is about 18° Bkr. strength. This is the first instance the writer has noticed in print of lime liquors of a definite barkometer strength. This is a new factor in limeyard control work but it has been successfully applied in many of the leading English and Continental chrome tanneries. Sodium sulphide solutions of a definite barkometer strength are employed in tightening the grain of pelts for chrome tanning, and the success of this sulphide treatment depends on three variable factors, *viz.*, time, concentration, and the percentage of the material on the pelt weight. The writer is convinced that there is great scope for the standardisation of these three vital factors in other processes of leather manufacture. There is very little fresh to report in the methods of deliming except the use of sodium bisulphite for this purpose.[22]

Tanning, Tanning Materials, Etc.

There have been no remarkable advances made in tanning or in the search for new materials. Considerable forests of oak and chestnut trees have been discovered in Burma[23] and these trees appear to be very rich in tannins. Samples taken and analysed have revealed a good workable content of tannin and a low non-tannin content. From tests made, it would appear possible to produce an extract from them containing about 80% of tannin. J. A. Pilgrim[24] has reported to the Government of India on the mangroves found in the Sundarbans Forest Division. F. Liebert[25] has traced the development of gas in oakwood extracts to the presence of a yeast which closely resembled *Saccharomyces apiculatus*. The infection was traced to the exposure of the concentrated extract to the air after being run out of the evaporator, and it affords an extraordinary instance of the selective growth of yeasts to the exclusion of bacteria and moulds.

Fresh attempts have been made to popularise the process known as electro-tanning. G. Grasser[26] has made a very complete study of the behaviour of the different tanning materials under the influence of an electric current. Most tannins have a negative charge, revealed by anodic migration. In most cases the migration is sluggish until some acid has been added to the solution. A certain amount of tannin is decomposed by the current and insolubles are formed. The purification or separation of the tannin constituents is not possible by means of electro-osmosis owing to secondary changes. Grasser claims that his experimental results

[22] *Leather Trades Rev.*, 1921, 954.
[23] *Ibid.*, 1921, 39.
[24] *Ibid.*, 1921, 378.
[25] *Collegium*, 1921, 76; *J.*, 1921, 312A.
[26] *Ibid.*, 1920, 17 *et seq.*; *J.*, 1920, 729A.

show that the passage of an electric current through tan liquors does facilitate tannage and special advantages accrue from the use of weak tan liquors. The Elektro-Osmose A.-G.[27] have been granted patents dealing with the tannage and weighting of hides and skins in connexion with the electro-osmotic process of tanning. The preliminary tannage is carried out in weak tanning liquors of sp. gr. 1·0007–1·0035 through which is passed a continuous current of 30 volts for 24 hours. The tannage is completed by immersing the hides in stronger liquors (sp. gr. 1·040) for 24 hours.

Several new suggestions have been made for accelerating the tanning process. A. Manvers[28] soaks and limes dried hides in an evacuated cylinder and then exposes the fleshed delimed hides to a high vacuum for ½ to 1 hr. A strong tanning solution from which all the air has been removed is pumped into the vessel under a pressure of 20–40 lb. per sq. in. The tanning process is stated to be accelerated[29] by placing the hides in a series of autoclaves each connected with a central filtering pit, through which the tanning liquors are circulated under a pressure of 3 atm. W. H. Ockleston and T. B. Carmichael[30] describe the preparation of a soluble starch for use in suspension pits or in the later stages of sole and heavy leather tannages. Manvers completes his tanning process by treating the hides with a weak glue or gelatin solution which is subjected alternately to high vacuum and high pressure. Various other patents have been granted for impregnating and waterproofing leather, *e.g.*, with commercial rubber cement.[31]

The British Boot, Shoe and Allied Trades Research Association has been busily occupied with the problem of weighted leathers. In the early part of the year a prominent tanner delivered a lecture[32] primarily intended for the boot and shoe trade and he gave utterance to some very sweeping assertions. He defended the weighting of sole leathers as adding to their wear and resistance. He claimed that insole leathers were heavily weighted because the boot manufacturers would not pay the price for an unadulterated article. In reply to criticisms of the insole leathers supplied he stated that if only the boot manufacturer would inform the tanner of his requirements in this respect, there was not an English tanner who could not fulfil them. The British Boot, Shoe, and Allied Trades Research Association has answered this challenge in a preliminary report issued on "Welted insole leathers."[33] The Association has defined the requirements of the boot manufacturer in respect

[27] E.P. 143,921 and 146,938; *J.*, 1921, 400A, 639A.
[28] E.P. 166,495 and 167,785; *J.*, 1921, 632A, 710A.
[29] E.P. 140,092; *J.*, 1921, 632A.
[30] E.P. 167,538; *J.*, 1921, 710A.
[31] U.S.P. 1,369,240; *J.*, 1921, 270A.
[32] *Leather Trades Rev.*, 1921,
[33] British Boot, Shoe and Allied Trades Research Assoc., July, 1921.

of insole leathers. Various samples of leathers sold for insoling purposes have been submitted to mechanical, physical, and chemical tests. The chemical analyses showed a wide variation in water-soluble and fat contents. It was observed that unsuitable leathers invariably contained a high percentage of water-soluble matter, which apparently rendered the fibres brittle and harsh. W. J. Chater and D. Woodroffe[34] have carried the investigation still further and find that the factor of cost is not always the criterion of quality. The water-soluble matter is very high in some tannages and they feel that there is an unnecessary waste of tanning material in the composition of many insole leathers. The Boot, Shoe and Allied Trades Research Association[35] has also carried out wearing tests to determine the relative wear-resistance of sole leathers. They find that the grain and flesh are both equally resistant to wear and that the middle tissue of the hide is the most resistant to wear. Their conclusions have been confirmed by the U. S. Bureau of Standards.[36]

The only other feature of interest in connexion with vegetable tanning is the manufacture of tanning extracts. Very little information has been divulged hitherto about this important branch of the tanning industry and yet it is most essential to modern sole leather tanning. C. T. Gayley[37] has contributed some notes on the best method of extracting chestnut wood. He recommends the step-up method of extraction, in which each decoction is heated with the wood for 30 mins. in an autoclave at a pressure of 2 atm., the temperature of extraction rising 10° F. (5° C.) for each decoction from 210°–280° F. (99°–135° C.). A. Harvey[38] has published a note on the yield of extract from tanning materials. B. B. Dhavale and S. R. Das[39] have determined the optimum temperature for the extraction of goran bark to be 55°–60° C. and 10-mesh to be the finest state of division practicable. The properties of sole and upper leathers for army boots discussed by Schiaparelli will be referred to later in the report.

Mineral Tannages.

There is no startling development to report in connexion with chrome and alum tannages, but there have been several interesting propositions in regard to iron tanning. The whole of the knowledge on that subject has been very thoroughly reviewed by D. D. Jackson and T. P. Hou,[40] who have advanced theories to account

[34] *J. Soc. Leather Trades Chem.*, 1921, **5**, 359 ; *J.*, 1922, 23A.
[35] *Pamphlet No.* 1, Sept., 1920.
[36] *Technol. Paper* 166, Aug. 21, 1920 ; *J.*, 1921, 230A.
[37] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 344 ; *J.*, 1921, 229A.
[38] *J. Soc. Leather Trades Chem.*, 1921, **5**, 115 ; *J.*, 1921, 440A.
[39] *Ibid.*, 1921, **5**, 229 ; *J.*, 1921, 709A.
[40] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 63 ; *J.*, 1921, 441A.

for the difficulties encountered in iron tannages. They affirm that iron is much more basic than chromium or aluminium, and the ferric hydroxide formed as a result of the hydrolysis of ferric salts is so unstable in the colloidal state that it is soon precipitated. Furthermore, the ferrous iron in solution, though easily partially oxidised, can only be completely oxidised with difficulty. It is necessary to convert the ferrous iron to the ferric state completely and then to keep it in the ferric state. Jackson and Hou give full directions for tanning leather with iron salts, and they claim that an iron-tanned leather, properly tanned, is not brittle on the grain and does not deteriorate on storing. The tannage can be effected by drumming for $1\frac{1}{2}$ hrs. in liquors of suitable basicity; $Fe(OH)SO_4$ is much too basic, since iron possesses a much greater basic character than chromium. Ferrous sulphate should be oxidised by means of chlorine, sodium nitrate and sulphuric acid, or a mixture of sulphuric and nitric acids and the basicity should be adjusted by the addition of sufficient alkali to yield a ratio of one OH equivalent to every 5 equivalents of the mineral acid radicle present. The tanned leather should be gradually neutralised so that the iron may be uniformly fixed in the pelt throughout its thickness. Before dyeing or finishing the leather it should be laid aside and allowed to dry out to minimise the chemical reactions between the iron in the leather and the finishing, dyeing, or mordanting materials which might react with the iron to give an undesirable colour. 4% of Fe_2O_3 is the minimum iron in an air-dried leather for a proper tannage. W. Moeller[41] contends that there appears to be no limit to the amount of iron which can be absorbed by hide. Iron salts show excessive electrolytic dissociation and the acid formed hydrolyses the hide tissue by prolonged contact. He found that 67% of the hide substance in a sample of hide powder was dissolved by strong iron solutions after 3 months' contact. Neutralisation of iron-tanned leather does not obviate this defect, which explains the decomposition of such leathers during storage.

O. Röhm[42] appears to have found a new iron salt, $FeSO_4Cl$, which is specially suitable for tanning. It is prepared by the action of chlorine on ferrous sulphate or by allowing mixtures of ferric chloride, sulphuric acid, and water, or ferric chloride, ferric sulphate, and water[43] to react and solidify. The product, $FeSO_4Cl,6H_2O$, is non-hygroscopic.

E. Kanet[44] tans hides by immersing them in a solution of ferric acetate in the presence of sodium chloride at a low temperature; the wet hides are heated to cause the separation of the basic salts upon and between the hide fibres.

[41] *Collegium*, 1921, 67; *J.*, 1921, 313A.
[42] E.P. 146,214; *J.*, 1921, 388A.
[43] E.P. 146,218; *J.*, 1921, 470A.
[44] U.S.P. 1,367,054; *J.*, 1921, 231A.

W. Moos and D. Kutsis[45] describe the production of flexible iron-tanned leather by means of ferrous sulphate waste liquor from the manufacture of cellulose and sodium nitrite.

The only new suggestion in regard to the manufacture of one-bath chrome tanning liquors has been that of C. F. L. Barber and P. R. Barker,[46] who propose to reduce solutions of chromic acid or bichromate and acid, with synthetic tan. Leather can be tanned by the two-bath process in which a strong solution of synthetic tan is used in the reduction bath.

Syntans.

There has been the customary crop of patents[47] for the production of new synthetic tans, but they are all of the familiar type, being condensation products of aromatic substances with or without the addition of formaldehyde. There have been several attempts to stimulate interest in syntans by scientific and technical articles describing their manufacture, use, and properties.[48] W. Moeller[49] has criticised the use of syntans as hydrolysing the pelt tissue.

Reference was made in last year's report[50] to the action of acids on hide powder, which Moeller considers to be first one of hydrolysis. Whatever the preliminary action of acids, there is every indication from the practical use of acids in leather manufacture that prolonged contact of hides with dilute acids results in the hydrolysis of the hide substance or collagen. Proteins are amphoteric compounds, combining with either acids or alkalis according to circumstances, but that does not preclude them from being decomposed by prolonged contact with excess of acid. Moeller contends that syntans have a very strong hydrolytic action on the hide. Whereas vegetable tannins diminish the amount of hide substance dissolved as a result of hydrolysis, synthetic tannins increase it. He urges the importance of using weak solutions of syntans and of thorough washing after tannage so that excess tannin may be removed. He implies that the free sulphonic acids in the syntans have really a bating action, and even suggests that the bating can be curtailed or eliminated where skins are to be tanned with synthetic tans. In a later paper W. Moeller[51] states that artificial tannins have only a slight preliminary tanning effect, but they contain a large amount of free sulphonic acids which exercise a bating action.

[45] G.P. 339,028 ; *J.*, 1921, 710A.

[46] E.P. 155,887 ; *J.*, 1921, 123A.

[47] G.P. 328,340 ; *J.*, 1921, 180A. G.P.336,895, 337,330, and 337,588 ; *J.*, 1921, 632A. G.P. 306,341 and 333,403 ; *J.*, 1921, 359A. E.P. 147,534 ; *J.*, 1921, 522A.

[48] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 20.

[49] *Collegium*, 1920, 520 ; 1921, 232 ; *J.*, 1921, 154A, 521A.

[50] *Ann. Repts.*, 1920, **5**, 365.

[51] *Collegium*. 1921, 232 ; *J.*, 1921, 521A.

Pure sulphonic acids were formerly recommended for bating. Renner u. Co.[52] claim to form quinones by oxidising the condensation products of aromatic substances and formaldehyde with different oxidising agents.

ANALYSIS.

Lime Liquors.

F. G. A. Enna[53] returns to the vexed question of the determination of alkali sulphides in lime liquors. Calcium polysulphides should be included in the estimation of sulphides. He discusses the formation of calcium polysulphide and thiosulphate from calcium sulphydrate, and points out the necessity for any sulphide estimation including the former but not the thiosulphate. The method of estimation depends upon the action of a current of carbon dioxide through the liquor. This separates the hydrogen sulphide from its alkali salts, but does not affect the thiosulphates and amino-acids. The hydrogen sulphide liberated is collected in copper acetate solution, the cuprous sulphide filtered off, and the residual copper determined volumetrically. A blank titration of the copper acetate solution is also made and the difference is due to hydrogen sulphide only. J. A. Wyler[54] has worked out a scheme for the determination of all the constituents of sodium sulphide. The combined sulphide, thiosulphate, thiocyanate, and sulphite is determined by titration with iodine. The estimation of sulphite and thiosulphate is based on expelling the hydrogen sulphide by boiling the solution with magnesium chloride solution. Sodium carbonate is estimated by precipitating with barium chloride, treating the precipitate with an excess of $N/1$ hydrochloric acid, and titrating back with $N/1$ soda. Sodium sulphate is determined by passing a stream of carbon dioxide through a solution of the sodium sulphide. The sulphur is filtered off and the sulphate in the filtrate precipitated with barium chloride.

Bating Materials.

The increasing use of tryptic enzyme mixtures for bating skins has rendered imperative the testing of commercial samples offered for the purpose. A. W. Thomas[55] suggests the determination of the tryptic activity by allowing the enzyme preparation to act upon an alkaline solution of casein. Aliquot portions of the mixture are pipetted at intervals into an acid solution, the unchanged casein filtered off and the amount of dissolved nitrogen determined in the filtrate. Measurements are made for the same sample with

[52] E.P. 146,166.

[53] *J. Soc. Leather Trades Chem.*, 1921, **5**, 131; *J.*, 1921, 480A.

[54] *Colour Trades J.*, 1921, **9**, 159.

[55] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 221; *J.*, 1921, 230A.

different times of digestion and compared with similar figures obtained with a standard material.

Tannin Analysis.

J. A. Wilson and E. J. Kern's[56] proposed new method of tannin analysis has given leather chemists one of the rudest awakenings they have had for some time. Fortunately there is evidence forthcoming not only to confirm their previous faith in the official methods but also to strengthen it. Wilson and Kern found in a certain upper leather yard in which all ingoing extracts were analysed over a period of three years and in which a careful check was maintained on the composition of the outgoing leather, that the tannin sold in the leather only amounted to half the tannin which had been consumed as extract, where the tannin had been estimated by the official methods, but the tannin consumed and the tannin found in the leather were equivalent for all practical purposes where the tannin was estimated by their new method. It has been claimed that some tannins combine more loosely than others with hide substance and are more easily removed by washing. J. A. Wilson and E. J. Kern[57] have investigated this claim by analysing gambier-tanned hide powder after 15, 25, and 50 washings, prepared by shaking a weighed amount of hide powder for 6 hrs. with a solution containing a weighed amount of gambier. After the repeated washings the tanned powder was dried and analysed to give the combined tannin which in turn provides the tannin content of the gambier according to the new method of analysis. The results were: After 15 washings, 7·87% tannin; 25 washings, 7·89%; 50 washings, 7·67%. These figures indicate that the number of washings has no material influence on the percentage of tannin found in various materials by the new method, and, further, that tannin once combined with hide cannot be washed out by any amount of washing that would be practical. Wilson and Kern evaporated solutions of non-tannins such as gallic acid, and showed that tannins were formed as demonstrated by their property of precipitating gelatin-salt solutions. The wash waters from the gambier analysis cited above were concentrated to small bulk and yielded an extra quantity of tannin. Wilson and Kern are of the opinion that the conversion of non-tannin into tannin is responsible for the time factor in tanning and the "ageing" of leather.

G. W. Schultz and T. Blackadder[58] dispute Wilson and Kern's claim that a definite compound is formed between tannin and collagen. They have shown that the finer particles of hide powder

[56] *Ann. Repts.*, 1920, **5**, 358.

[57] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 75; *J. Ind. Eng. Chem.*, 1920, **12**, 1149; *J.*, 1921, 52A.

[58] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 654; *J.*, 1921, 480A.

take up more tannin than the coarser particles and they are lost in washing. Schultz [59] has confirmed these results and shown that the wash waters from hide powder tanned with chestnut extract contained an appreciable amount of tannin which could not have been formed from non-tannins since they were not concentrated. A solution of chestnut extract was diluted to the extent of the wash waters from the Wilson-Kern method of analysis and this dilute solution failed to give the tannin reaction with gelatin-salt reagent. After concentrating to small bulk and diluting again, however, the solution gave the tannin test. Schultz contends that the colloidal state of the tannin material influences the incidence or absence of a precipitate with the gelatin-salt reagent. The concentration of dilute solutions causes the tannins to aggregate and thus give a positive test with the gelatin-salt reagent. The amount of tannin estimated by Wilson and Kern's method varies according to the amount of hide powder used for detannisation. There is no essential difference between the official method and the new method except that 15 washes remove some of the loosely combined tannin and give a lower tannin result. The different methods are based on absorption. If Wilson and Kern's assumptions were correct the amount of absorbed matter after thorough washing would be independent of the amount of hide powder used. Three main factors influence the absorption of tannin by hide powder, *viz.* :—the amount of powder, the concentration of the tannin solution, and the volume of solution. The official method of tannin analysis affords the maximum absorption of tannin. These are the views of Schultz, and Wilson [60] has subjected them to severe criticism.

H. R. Procter,[61] in reviewing the subject of tannin analysis, contends that the discrepancies in analyses are attributable to several variable factors which have been neglected somewhat in the past. There is no criterion of optical clearness and he cites instances of 5 or 6% of additional insolubles having been removed by repeated filtration. He implies that filtration by the Berkefeld filter candle should be made compulsory, and in this particular he is supported by the work of J. G. Parker and J. T. Terrell,[62] who have shown the superiority of the filter candle to filter paper for the determination of soluble matter in tanning extracts. Filter paper was shown to absorb soluble matter even when a considerable quantity (200 c.c.) was rejected before evaporating to dryness. Procter suggests that the acidity of solutions may influence the amount of insolubles and non-tans. He thinks that a great deal

[59] *Ibid.*, 1921, **16**, 349; *J.*, 1921, 858A.

[60] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 622, 631, 637; *J.*, 1922, 24A.

[61] *Ibid.*, 1921, **5**, 219.

[62] *J. Soc. Leather Trades Chem.*, 1921, **5**, 112; *J.*, 1921, 440A.

of research is needed before any definite conclusion can be drawn as to whether a complete separation of non-tans would give a truer picture of the practical value of any material. It is acknowledged that the present method of tannin analysis is imperfect, but in the opinion of most it is a better guide to the value of tanning materials than the Wilson-Kern proposed method.

There have been several papers on qualitative analysis of tannins, the most valuable of which deals with Indian tanning materials. W. R. Atkin and K. H. Hassan[63] have tabulated the reactions of a number of these, and this work forms a valuable contribution to our knowledge.

Leather Analysis.

The most important change or development in leather chemistry is that at present taking place in leather analysis. The application of hydrogen-ion determinations to all branches of leather manufacture was referred to last year[64] but the changes in leather analysis had not then been made. The American leather chemists have carried out a series of very exhaustive investigations into the question of the sampling of leather and its preparation for analysis,[65] and they recommend that samples should be cut from the side, belly, shoulder, and butt as these are the most divergent in composition. These samples are subdivided by sawing or planing. M. P. Chambard,[66] reporting on the work of a committee of the French section of the Society of Leather Trades' Chemists, has been able to show that there are zones of similar composition in the hide, and he suggests that samples should be cut from the juncture of the bend with the shoulder, as this represents fairly average composition of the whole side. He recommends that the sample be subdivided by rasping except for the nitrogen estimation, when it should be cut up with a knife or razor.

The determination of the water-soluble matter in vegetable-tanned leathers is a matter of urgent importance, since it has been established that most leathers contain a large preponderance of water-soluble matter. C. Schiaparelli[67] claims that the present method of determining water-soluble matter gives results which are not comparable with those of actual wear, and he contends that tests should be made by immersing whole soles in water for 72 hours. The American chemists[68] are very doubtful whether the maximum amount of water-soluble matter is extracted at 45° C.—the present official temperature for the extraction of water-soluble

[63] *Ibid.*, 1921, **5**, 347; *J.*, 1922, 24A.
[64] *Ann. Repts.*, 1920, **5**, 360.
[65] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 394; *J.*, 1921, 781A.
[66] *J. Soc. Leather Trades Chem.*, 1921, **5**, 313.
[67] *Ibid.*, 1921, **5**, 44; *J.*, 1921, 270A.
[68] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 491; *J.*, 1921, 819A.

matter from leather. A large amount of investigational work carried out in this country on the question of water-soluble matter in leather has been communicated privately to the writer, and seems to indicate that 1 litre of percolate in 3 hours at 45° C. is insufficient. In several instances a further 4–6% was obtained by extracting a second 1000 c.c.

It is proposed to change the solvent for extracting the grease from leathers and make chloroform official.[69] The American chemists propose to adopt chloroform as the official solvent after the report of a committee to the effect that chloroform is probably the most reliable solvent for grease in leather. It has long been recognised that petroleum spirit is a very imperfect grease solvent. In the determination of unsaponifiable matter in the analysis of degras, the oxidised oils and fatty acids will not dissolve in petroleum spirit and alcohol is added to assist that solvent. There is no doubt that there are many serious errors in the fat estimations which have been conducted on leather samples, and this new solvent will afford a great improvement.

Slight improvements have been made in the Kjeldahl estimation of nitrogen in leathers. It is now recognised that 0·7 g. is insufficient for accurate work, and J. G. Parker[70] and M. P. Chambard[71] recommend the use of 1¼–2 g. The influence of the atmospheric humidity[72] in moisture determinations has led Chambard to use covered vessels for that determination. The estimation of free sulphuric acid in leather[73] is still a vexed problem which does not appear to approach any definite solution. C. Immerheiser claims that his ether-sulphuric acid method estimates with a fair degree of accuracy the amount of free sulphuric acid purposely added to the leather. T. P. Hou[74] has drawn attention to some errors in the sodium peroxide method of determination of chromium in chrome-tanned leather which can be obviated by evaporating the sodium chromate solution to small bulk to decompose any remaining peroxide.

Theory of Tanning, etc.

Chemistry of Tannins.

K. Freudenberg[75] and his pupils are carrying on the valuable work initiated by Emil Fischer. The tannins of the woods of the

[69] *J. Soc. Leather Trades Chem.*, 1921, **5**, 306.
[70] *Ibid.*, 1921, **5**, 304.
[71] *Ibid.*, 1921, **5**, 313.
[72] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 547.
[73] *Collegium*, 1920, 465 ; *J.*, 1921, 53A. *Ibid.*, 1921, 132 ; *J.*, 1921, 441A.
[74] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 367 ; *J.*, 1921, 231A.
[75] *Ber.*, 1921, **54**, 1205 ; *J.*, 1921, 521A.

edible chestnut[76] and native oak[77] have been shown to contain quercitin, glucose, and ellagic acid. Native oak tannin has been purified and hydrolysed into ellagic acid, quercitin diglucoside, and 50% of a rich orange-yellow tannin substance the nature of which remains to be determined. Freudenberg[78] has summarised the work of Emil Fischer on depsides and tannins and describes how gallotannic acid, glucogallin, and fully-methylated gallotannic acid were synthesised. One of Fischer's methods of synthesis for the preparation of partially acetylated glucose derivatives consisted in combining two molecules of acetone with one of dextrose to form a diacetoneglucose. The free hydroxyl group was combined with an acid chloride and the acetone was split off one molecule at a time. The most recent developments in tannin investigation are along the lines of analysis by means of tannase which has been used by Fischer, Freudenberg, and Vollbrecht.[79]

Chemistry of Hide and Gelatin.

J. Loeb[80] has shown that the amount of any ion entering into combination with a protein, depends on the hydrion concentration of the protein, and therefore the ratios in which different ions combine with proteins must be compared for the same hydrion concentrations. This disposes of the Hofmeister series of ion effects. Gelatin is isoelectric at $p_H = 4{\cdot}7$. At a $p_H > 4{\cdot}7$ it can combine with cations only, at a $p_H < 4{\cdot}7$ it can combine with anions. The quantity of anion or cation in combination with the protein is a function of p_H. Acids and bases combine with proteins in the same way as they combine with crystalline compounds, by the forces of primary valency, and in this respect he states that the chemistry of colloids in no way differs from the chemistry of crystalloids. The laws of general and physical chemistry provide a quantitative theory not only of the chemical behaviour of proteins but also of some of the physical properties. In further work, Loeb has shown that at the same p_H the effect of ions on swelling, osmotic pressure, and viscosity of gelatin depends only on the sign and valency of the ions, and univalent ions of the same sign have practically the same effect.

W. R. Atkin[81] has described various curves obtained for the swelling of hide by alkalis and other materials used in the liming process. Weighed quantities of hide powder were treated with alkaline solutions of varying strengths, and allowed to stand for

[76] *Ibid.*, 1921, **54**, 1695; *J.*, 1921, 781A.
[77] *Naturwiss.*, 1920, **8**, 905.
[78] *Collegium*, 1921, 10; *J.*, 1921, 312A.
[79] *Cf. Collegium*, 1921, 468; *J.*, 1922, 67A.
[80] *J. Soc. Leather Trades Chem.*, 1921, **5**, 137; *J. Gen. Physiol.*, 1921, **3**, 391, 557; *J.*, 1921, 314A.
[81] *J. Soc. Leather Trades Chem.*, 1921, **5**, 306.

2 hrs. to settle, after which the volume of hide powder was measured in a burette. This is suggested as a works method of limeyard control. It was found that the addition of salt up to certain proportions increased the swelling in the limes.

G. Grasser[82] finds that organic acids behave very similarly in regard to their swelling effects on pelt, whilst A. A. Claflin[83] obtains greater plumping power with lactic acid. There have been suggestions for adopting Claflin's method of measuring the plumping power of a tanning solution. It consists in shaking 5 g. of hide powder with 200 c.c. of the solution, allowing to stand 24 hrs., filtering through a cotton cloth without squeezing, draining completely and measuring the volume of filtrate obtained. The less filtrate obtained the greater the plumping power of the solution. G. D. McLaughlin[84] has obtained most swelling on fresh hide, with organic acids at a concentration greater than $N/20$. Additional swelling was obtained by further soaking in lactic acid. He warns tanners against the use of salts of heavy metals for curing or disinfection since these salts very much repress the swelling. The rapid changes occurring in the hide after the animal's death have already been referred to.

W. Moeller[85] emphasises the importance to the theory of tanning of the part played by ammonia. Hide powder gives up 1·56% of ammonia when distilled with potash and it contains 0·75% of hydrolysed protein which contains 3% of ammonia. Ammonia hydrolyses pelt to a less extent than calcium or sodium hydroxides.

Chrome Liquors, Chrome Tanning, etc.

Carbon dioxide functions as an acid in a chrome liquor so that the addition of acid to the boiling liquor in the basicity determination is in error. D. Burton and A. M. Hey[86] propose to obviate this error by running the $N/2$ alkali into the cold, diluted chrome liquor in presence of phenolphthalein, and that the addition should be continued during the period of heating up to the boiling point and then until the pink colour persists after boiling for 1 min. L. Meunier[87] concludes from some experiments on the action of sodium carbonate on solutions of chrome alum that solutions of chrome alum not only undergo hydrolysis but also that the basic chromium salts polymerise with increase in time and temperature; further, that the neutralisation of the sulphuric acid by the sodium carbonate is accompanied by setting free carbonic acid which is more or less

[82] *Collegium,* 1920, 353, 405, 456, 512; *J.*, 1921, 154A.
[83] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 234; *J.*, 1921, 230A.
[84] *Ibid.*, 1921, **16**, 295; *J.*, 1921, 669A.
[85] *Collegium,* 1921, 265; *J.*, 1921, 554A.
[86] *J. Soc. Leather Trades Chem.*, 1920, **4**, 272; *J.*, 1921, 19A.
[87] *Le Cuir,* 1921, **10**, 84.

eliminated by heating and agitation. The appearance of a precipitate results from the action of sodium carbonate both as a neutralising agent and as a coagulating agent of the colloidal solution of chromium hydroxide or of the polymerised chromium salts. D. Burton[88] has made a theoretical study of the mechanism of the neutral salt effect in chrome tanning and suggests that the effect of neutral salts on chrome tanning liquors is to decelerate the penetration of the chromium compounds by a blockading action of the neutral salt. The combined action of the acid and salt will cause a change in the swelling. Neutral salts cause more acid to be taken up by the pelt, and therefore a more basic chromium salt will remain in the tanning liquor. The more basic a chromium salt the lower its rate of diffusion and the more slowly will the pelt be penetrated by the chromium compounds. This has been demonstrated in practice. Used chrome tanning liquors do not tan as quickly as fresh liquors, and if the liquor has been used several times then the accumulation of salts seriously retards the tanning process. In collaboration with A. Glover,[89] the same author has attempted to determine the influence of neutral salts on the absorption of the acid and chromium from chrome tanning solutions by gelatin. Neutral salts decrease the diffusion of the chromium into gelatin and the order of retardation is the same as that of the degrees of hydration. Neutral chlorides cause an increase in the amount of acid absorbed, whereas sulphates cause a decrease. The importance of these results will be realised since sodium chloride is often used in chrome tanning liquors and neutral chlorides or sulphates, or both, are always present. E. Griliches[90] considered that chromium salts split up into a basic portion and a chromo-sulphuric acid. E. Stiasny[91] contests this view and asserts that they hydrolyse into a basic chromium salt and free sulphuric acid. In the early stages of chrome tanning there is a greater absorption of the free acid, in the later stages an increasing and finally preponderant absorption of the basic portion. Griliches[92] has replied to Stiasny but has not brought forward any fresh facts.

The analysis of chrome tanning liquors has received more attention than usual. W. Klaber[93] suggested a new method of expressing basicity nearly two years ago, and there have been several fresh suggestions since then by E. Griliches[94] who thinks that in $Cr : SO_4 = 52{\cdot}1 : X$, X should be termed the acidity. K.

[88] *J. Soc. Leather Trades Chem.*, 1921, **5**, 183, 192; *J.*, 1921, 669A.
[89] *Ibid.*, 1921, **5**, 187; *J.*, 1921, 669A.
[90] *Ann. Repts.*, 1920, **5**, 367.
[91] *Collegium*, 1920, 479; *J.*, 1921, 53A.
[92] *Ibid.*, 1921, 127; *J.*, 1921, 441A.
[93] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 622.
[94] *Collegium*, 1921, 127; *J.*, 1921, 441A.

Schorlemmer[95] suggests that the basicity should be expressed as the percentage of chromium fully saturated with hydroxyl groups. G. Grasser[96] has plotted the basicity expressed according to Schorlemmer's method against the tanning intensity and finds a maximum for the salt $Cr_4(SO_4)_3(OH)_6$. A rapid method of determining the chromium in a chrome tanning liquor has been devised by A. W. Thomas and M. W. Kelly[97] in which an immersion refractometer is used and the readings compared with tables compiled from pure solutions of known strength. B. B. Dhavale and S. R. Das[98] observed last year that the end-point of the alkalimetric titration of chrome tanning liquors for acidity according to the Procter-McCandlish method was influenced by temperature and the rate at which the alkali was run in. Additions of sodium chloride caused a marked increase in the acidity and they recommended the addition of 49 g. or more of pure sodium chloride in that alkalimetric titration, using 400 c.c. of diluted liquor containing 0·1747 g. of chromium. A. W. Thomas and S. B. Foster[99] have confirmed these experiments and think that 50 g. of sodium chloride would be enough. J. E. Pickering[100] finds difficulty in the determination of the basicity of chrome tanning liquors in dark weather and proposes the use of the following procedure. The alkalimetric titration is carried out in a beaker placed on a white tile immediately behind which is a "half-watt" lamp, covered with an opal shade, so arranged that the rays of light strike upwards through the liquor. The titration is continued until the liquid assumes a yellowish-pink colour.

K. Schorlemmer[101] finds that the use of commercial hydrochloric acid containing more than 0·0015% of arsenic is uneconomical in the reduction bath of the two-bath chrome tanning process. The action of hydrochloric acid on sodium thiosulphate solutions is twofold. Thiosulphuric acid may be liberated and immediately decompose into sulphurous acid and free sulphur, or the thiosulphate may polymerise and form sodium pentathionate:—

(1) $Na_2S_2O_3+2HCl=2NaCl+H_2SO_3+S$.

(2) $5Na_2S_2O_3+6HCl=2Na_2S_5O_6+6NaCl+3H_2O$.

According to Schorlemmer the presence of arsenic in the hydrochloric acid catalyses the second reaction, and thus the reduction is impeded or it may be prevented altogether. More acid is required to effect the reduction. It is probable that Stiasny will contest this view since he has already, in conjunction with S. R. Das,

[95] *Ibid.*, 1920, 536; *J.*, 1921, 155A.

[96] *Ibid.*, 1921, 319; *J.*, 1921, 669A.

[97] *J. Amer. Leather Chem. Assoc.*, 1920, **15**, 620; *J.*, 1921, 481A.

[98] *J. Soc. Leather Trades' Chem.*, 1920, **4**, 225; *J.*, 1920, 758A.

[99] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 61; *J.*, 1921, 441A.

[100] *J. Soc. Leather Trades' Chem.*, 1921, **5**, 177; *J.*, 1921, 669A.

[101] *Collegium*, 1921, 430; *J.*, 1922, 24A.

advanced a different theory as to the action of the acid and thiosulphate in the reduction bath.

Glue, etc.

There is not much to report in this section although there are signs of scientific activity in this branch of the industry. The glue and gelatin manufacturers are apparently alive to the need for the application of science to their trade judging by the advertisements in the trade Press. They are very anxious to have fully qualified practical chemists in charge of their plants or assisting in controlling the manufacture. Several patents have been granted for fresh methods of and apparatus for extracting glue and gelatin from the usual material,[102] fish refuse.[103] Vegetable glues, prepared by the action of alkali on starch, are described by E. Stern,[104] and also in patents granted to The Perkins Glue Co.[105] The testing of glues has provided more scope for scientific work, and D. R. Fraser[106] has worked out a test for comparing the tensile strengths of glues: 25 g. of glue is dissolved in 100 c.c. of water and 0·3 c.c. of the solution is employed in gluing together two halves of a pitch-pine briquette, which are pulled apart in a machine after the glue has had 24 hrs. to set. A good glue has a tensile strength of over 300 lb. per sq. in.

S. E. Sheppard and S. S. Sweet[107] have measured the modulus of rigidity of gelatin jellies under torsion and find it to follow Hooke's law nearly to the breaking point, the elastic limit nearly coinciding with the tenacity. The elasticity is not a simple function of the hydrogen-ion concentration in the case of acid jellies. Alcohol and glycerol increase the jelly strength up to a certain strength. In another communication, the same authors[108] describe a device to determine the setting and melting points of gelatin. A stream of air bubbles, under constant pressure, is passed through the gelatin solution which is cooled with ice-water. A thermometer is immersed in the solution with its bulb adjacent to the air inlet, and the temperature at which the bubbles cease to pass is taken as the setting point. After sufficient under-cooling the jelly is heated gradually, and the point at which the bubbles again pass is taken as the melting point.

A. Gutbier, E. Sauer, and M. Brintzinger[109] describe a method for determining the sulphurous acid in bone glue and leather glue.

[102] U.S.P. 1,364,904; *J.*, 1921, 155A. G.P. 337,178; *J.*, 1921, 632A.
[103] E.P. 155,863; *J.*, 1921, 121A.
[104] *J. prakt. Chem.*, 1920, **101**, 308; *J.*, 1921, 234A.
[105] U.S.P. 1,378,078 and 1,378,105-6; *J.*, 1921, 670A.
[106] *Analyst*, 1921, **46**, 284; *J.*, 1921, 632A.
[107] *J. Amer. Chem. Soc.*, 1921, **43**, 539; *J.*, 1921, 313A.
[108] *J. Ind. Eng. Chem.*, 1921, **13**, 423; *J.*, 1921, 554A.
[109] *Kolloid-Zeits.*, 1921, **29**, 130; *J.*, 1921, 709A.

The total acid in bone glue is titrated with $N/10$ sodium hydroxide solution. The sulphurous acid, which is all free, is titrated with $N/10$ iodine solution. Leather glue contains its sulphurous acid combined, and it also may contain formaldehyde. The glue solution is acidified with phosphoric acid and distilled in a current of steam and carbon dioxide, the vapours being passed into iodine solution. V. Froboese[110] has modified the Haas method of distilling over sulphurous acid. He distils it into a known quantity of sodium bicarbonate solution, oxidises it to sulphuric acid with hydrogen peroxide, and titrates the excess of alkali with hydrochloric acid in presence of methyl orange.

W. M. Clark and his collaborators[111] have described the preparation of high-grade casein by heating skimmed milk to 93° F. (34° C.) and adding dilute hydrochloric acid. R. H. Shaw[112] has worked out methods of analysis of casein for moisture, ash, sugar, phosphorus, and calcium. Numerous patents involve the use of casein for the production of plastic cements or hardening materials.[113]

[110] *Chem. Zentr.*, 1921, **92**, IV., 225 ; *J.*, 1921, 641A.

[111] *J. Ind. Eng. Chem.*, 1920, **12**, 1163 ; *J.*, 1921, 53A.

[112] *Ibid.*, 1920, **12**, 1168 ; *J.*, 1921, 53A.

[113] U.S.P. 1,360,356 ; *J.*, 1921, 53A. E.P. 169,405 , *J.*, 1921, 782A. U.S.P. 1,391,768-770 ; *J.*, 1921, 820A.

SOILS AND FERTILISERS.

By E. J. Russell, F.R.S.,

Director of the Rothamsted Experiment Station.

As in previous years, the report deals with the aspects of agricultural chemistry directly affecting the chemist concerned with farmers' or manufacturers' problems; it does not attempt to treat the more academic aspects of the subject, these being discussed in the Report to the Chemical Society. In the present account attention will be directed mainly to the work on fertilisers and on soils: feeding stuffs and dairy produce are dealt with in the section on Foods.

The past year has seen most of the British Agricultural Research Stations settle down to post-war conditions and there has been a significant pronouncement by the Minister of Agriculture emphasising "the determination of the Government to pursue the policy of education and research as the most permanent method of improving agriculture," and further pointing out that "even in these times of financial distress when every item of national expenditure is being closely overhauled it set aside a further provision of funds for these purposes." This pronouncement was not only accepted without demur by farmers, but was in no way in advance of the attitude taken up by their very comprehensive National Farmers' Union, who consented to forego the promised subsidy for corn on condition that a sum of £1,000,000 was set aside for research and education, particular stress being laid on research. Coming as this did from the farmers themselves in a time of financial depression, it affords convincing proof of the progressive spirit now abroad in the countryside and of a readiness to co-operate with men of science, which had long been patent to close observers, but has not hitherto been so publicly demonstrated.

The Research Stations now established in Great Britain are:—

Rothamsted: Soils, plant nutrition, and plant pathology.
Cambridge: Plant breeding, animal nutrition.
Oxford: Agricultural economics.
Imperial College, South Kensington: Plant physiology.
Reading: Dairy.
East Malling, Kent: Soft fruit.
Long Ashton, Bristol: Hard fruit and cider.
Aberystwyth: Plant breeding for wet climates.
Aberdeen: Animal nutrition,

with smaller stations at Cheshunt and at Ormskirk for the glass-house industry and for potatoes respectively.[1]

In addition to these an important private experimental station has been set up by the Olympia Agricultural Co., under the chairmanship of Mr. Joseph Watson, of which Professor C. Crowther has been induced to accept the Directorship. He has gathered at Offchurch an able staff, including Messrs. C. T. Gimingham, H. Hunter, F. H. Billington, E. Paul, R. H. Carter, and others, and he has the advantage possessed by no other station of having no fewer than six large estates in different parts of the country, on which experimental work can be carried out. A first report has already been published covering the period April, 1919—June, 1921[2]: it deals with the soils of the estates, with plant breeding, and with rations for cattle. The research programme is planned on generous lines and useful results may certainly be expected.

Fertilisers.

The past season saw a steep fall in prices of farm produce and few farmers would come out of it without financial loss—in some cases serious loss. This means, of course, enforced economy in every direction, and in spite of the great reduction in price of fertilisers it is doubtful whether the war level of consumption will be maintained. When the transition period is over, however, it is hoped that farmers will once more be in a position to farm intensively, and in the meantime much valuable information is being gleaned which is helpful now and will prove of great assistance when better times come.

An interesting summary of the statistics of consumption of fertilisers before and after the war is given by H. J. Bailey.[3] Supplies of phosphates and of nitrogenous fertilisers increased during the war, as also did the productive capacity of the works. Fear of fertiliser shortage seems to be banished indefinitely.

Nitrogenous Fertilisers.

Synthetic nitrogenous fertilisers continue to attract much attention, and a summary of their agricultural properties has been issued.[4]

In regard to supplies, a statistical supplement to the Report of the Nitrogen Products Committee has been issued, bringing the tables up to the end of 1920. This publication gives the best

[1] For an account of these Stations and their work see the very interesting *10th Report of the Development Commission*, 1920. H.M. Stationery Office. 2s.

[2] *Olympia Agricultural Co., Ltd., Research Dept., 1st Annual Report*, 1921.

[3] *J.*, 1921, 246R.

[4] E. J. Russell, *J. Min. Agric.*, 1921, **27**, 1037.

available statistical information.[5] It is unnecessary to go into details of the various countries: reference will be made only to Great Britain and Germany. The English company (Synthetic Ammonia and Nitrates, Ltd.) is now working a semi-large scale plant producing 1 ton of ammonia per day, soon to be increased to 2 tons.[6] Another company intends to erect a works in Cumberland with an initial output of 50,000 tons of sulphate of ammonia per annum, using the Claude process.[7]

Descriptions have been published of the Haber process, as operated at Merseburg (Saxony),[8] where the works when completed will have a capacity of 800 tons NH_3 per day; of the ammonia oxidation process carried out at Höchst[9]; and the processes used at the ill-fated Oppau works.[10] The German production, when the plant is fully working, is estimated[11] at 500,000 tons of nitrogen per annum, of which 300,000 is from synthetic ammonia, 100,000 from cyanamide (not necessarily used as such, but partly converted into other substances), and 100,000 from gas and coke-oven plants. Many attempts have been made to utilise ammonium nitrate. The difficulties in regard to its hygroscopic nature were dealt with by admixture with various substances which it was hoped would not only overcome the hygroscopicity but would entirely destroy the explosive properties of the nitrate. A typical example is as follows: a hot, concentrated solution of ammonium nitrate is mixed with hot potassium chloride or other fertiliser salt; interaction ensues, and after evaporation a dry cake is finally obtained which can be milled.[12] Other German patents have been taken out, the purpose or advantage of which it is not easy to see.[13]

A number of the German patents dealt with the preparation of a non-explosive fertiliser[14] from ammonium nitrate, but in view of what has since happened at Oppau[15] they must be regarded with suspicion.

It seems improbable that ammonium nitrate will play any important part as a fertiliser in our time, though it has valuable properties and has been used with advantage in this country.[16]

[5] *J.*, 1921, 285R.

[6] *J.*, 1921, 240R.

[7] J. H. West, *J.*, 1921, 240R.

[8] J. R. Partington, *J.*, 1921, 144R.

[9] *J.*, 1921, 185R.

[10] J. R. Partington, *J.*, 1921, [illegible]R.

[11] *J.*, 1921, 237R.

[12] Badische Anilin u. Soda Fabr., E.P. 145,036; *J.*, 1921, 443A. Also Akt.-Ges. für Anilin-Fabr., E.P. 146,259 and 145,582; *J.*, 1921, 232A.

[13] *Cf. J.*, 1921, 315A.

[14] *E.g.*, G.P. 336,876; *J.*, 1921, 596A.

[15] *J.*, 1921, 381R.

[16] E. J. Russell, *J. Min. Agric.*, 1919, 25, 1332

German opinion is now in favour of urea as a nitrogenous fertiliser; it is concentrated and therefore economical of transport; it has no harmful effects in the soil, or, so far as can be seen, on crops, even when applied in excessive quantities.[17] A number of patents have been taken out for utilising this substance in mixed fertilisers,[18] and a method of estimation has been based on its reaction with oxalic acid.[19]

From the manufacturer's point of view there is something to be said for the production of ammonium chloride, as this can be combined with the ordinary ammonia-soda process for preparing alkali. Instead of employing the same ammonia over and over again, new supplies of synthetically prepared ammonia are used and ammonium chloride obtained as a product.[20] It is claimed to be a further advantage to oxidise part of the ammonia and absorb the nitrogen oxides by the sodium bicarbonate. Further details of the method have also been patented.[21] The fertiliser tests with ammonium chloride are not yet completed.

Ammonium bicarbonate could no doubt be prepared on the large scale if it were found suitable. It has the advantage of leaving no acid residue in the soil, but against this is to be set the serious defect that it is volatile and therefore subject to loss. To prevent or reduce the loss the proposal is made that it should be mixed with 5–10% of anhydrous sodium sulphate or 10% of magnesium sulphate.[22]

The standard ammoniacal fertiliser is, however, sulphate of ammonia. The usual grade as made by good firms is guaranteed to contain $25\frac{1}{4}\%$ of NH_3, but a little free acid is present which interferes with the removal of the last fraction of moisture. A "neutral" form is now being produced which can be better dried, and therefore assumes a more friable condition—a great advantage from the farmer's point of view as it facilitates spreading. Further, in absence of acid the bags are not rotted. The removal of water raises the ammonia content and a guarantee of $25\frac{1}{2}\%$ is given. The details of the manufacture at the South Metropolitan Gas Works[23] and at Bedford[24] are published.

Field experiments show that the fertiliser value of cyanamide is not quite as high as that of ammonia or of nitrate. One cause of this is the presence of dicyanodiamide, which is toxic to plants and certain micro-organisms. Unfortunately the conversion of

[17] *J.*, 1921, 237R.
[18] *J.*, 1921, 782A.
[19] E. B. Johnson, *J.*, 1921, 126T.
[20] Badische Anilin u. Soda-Fabrik, E.P. 144,659; *J.*, 1921, 522A.
[21] Badische Anilin u. Soda-Fabrik, E.P. 145,038; *J.*, 1921, 782A.
[22] Badische Anilin u. Soda-Fabrik, G.P. 310,055; *J.*, 1920, 233A.
[23] E. V. Evans, *Gas J.*, 1920, **152**, 515; *J.*, 1921, 3A.
[24] J. B. Hansford, *Gas World*, 1921, **75**, 243; *J.*, 1921, 733A.

cyanamide to dicyanodiamide appears to be facilitated by the presence of ordinary superphosphate, although it seems that the reaction proceeds only in presence of moisture: a dry cyanamide is said to be unaffected by dry superphosphate.[25]

A method for estimating dicyanodiamide in cyanamide and mixed fertilisers has been devised, based on the fact that dicyanodiamide is precipitated by silver picrate, whilst cyanamide and urea are not.[26] The effectiveness of cyanamide is said to be increased when mixed with the soil disinfectant "Humus-carbolineum," prepared from lignite,[27] though the reason of this is not quite clear.

Phosphates.

The chief phosphatic manures are superphosphate, basic slag, mineral phosphates, and bones.

Superphosphate is used to a larger extent than the others. Two interesting papers have appeared this year—one by W. Packard,[28] describing the various mineral phosphates used in the manufacture and giving much useful information not easily obtainable elsewhere; the other dealing with the phenomena of "reversion." This term is used to denote the change from soluble to insoluble phosphate occurring under certain circumstances, especially when iron and alumina are present. It appears that the effect of these two metals is not appreciable when they occur as sulphates, but it becomes very marked if sufficient of the oxides remains as such and escapes conversion into sulphates.[29]

Instead of sulphuric acid it has been suggested to use nitric acid for the manufacture of superphosphate. Raw phosphate is mixed with finely ground potassium sulphate and treated with nitric acid, this is then dried and ground: the mixture consists of monocalcium phosphate, potassium nitrate, and gypsum, and is claimed to be non-deliquescent.[30]

Basic slag is used to a less extent than superphosphate, partly because it is slower in action and therefore less suitable in the Eastern counties, and partly because it is only a by-product in the manufacture of steel and therefore its output is limited. At the present time the demand is greater than the supply: no less than 15,769 tons was imported during the six months ending

[25] R. N. Harger, *J. Ind. Eng. Chem.*, 1920, **12**, 1111; *J.*, 1921, 93A.

[26] E. B. Johnson, *J.*, 1921, 125T; also *J. Ind. Eng. Chem.*, 1921, **13**, 533. R. N. Harger, *J. Ind. Eng. Chem.*, 1920, **12**, 1107; *J.*, 1921, 92A.

[27] M. Popp, *Deuts. Landw. Presse*, 1920, **90**, 617; *J.*, 1921, 522A.

[28] *J.*, 1921, 288R, 304R.

[29] B. Neumann and K. Kleylein, *Z. angew. Chem.*, 1921, **34**, 77; *J.*, 1921, 271A.

[30] Chem. Fabr. Rhenania, and G. A. Voerkelius, E.P. 148,242; *J.*, 1921, 782A.

March 31st, 1921.[31] But it plays so important a part in British agriculture that the Ministry of Agriculture has set up a Committee to deal with problems connected with the material. Recognising that the output cannot be increased, the Committee has discussed the possibility of enrichment. Addition of mineral phosphates in the ladle was unsatisfactory, the change in the mineral being too slight to justify the process. The Committee is considering the possibility of utilising iron ore containing more phosphorus and of introducing into the blast-furnace the lowest grade of slag.[32]

The most important problem now is to discover whether any relationship can be traced between the fertiliser value of the slag and the solubility of the phosphate in some chemical reagent such as a 2% solution of citric acid. The basic open-hearth slags form by far the largest portion of the supply, but their solubility in this reagent varies from 20% or less to 90% of the total phosphate present, according as fluorspar is or is not added in the furnace. On the chemical side F. Bainbridge finds that calcium phosphates become insoluble on fusion with fluorspar and concludes that apatite, $3Ca_3(PO_4)_2,CaF_2$, is formed in open-hearth slags; while in soluble slag the constituent is silico-carnotite, $Ca_3(PO_4)_2,Ca_2SiO_4$, which can be obtained by fusing dicalcium silicate with tricalcium phosphate, and is completely soluble in citric acid. The result of re-fusing a slag without addition of lime is to increase considerably the solubility of the slag.[33]

On the field side, however, comparison of various slags on grassland showed less difference than was indicated by their solubilities: a slag of 45% solubility giving approximately as good a result as one of 90% solubility. Below 45% the results were not so good.[34] There appears, however, to be some difference in the crop; Bainbridge found that insoluble slag gave better results in pot experiments when applied in autumn than in spring; but while it increased the crop, it did not increase the phosphorous content of the grain and the straw as did the soluble slag.

There is the possibility also of differences of action in the soil. Slag produces a striking improvement in grassland but its effect does not end here. When the grass is subsequently ploughed up and converted into arable a marked gain in fertility is revealed. In the Suffolk experiments there was not only an important increase in live weight of sheep grazing on the slagged plots in comparison with those on the unslagged land during the eight years of grass husbandry, but at the end of the period the slagged plots contained

[31] *J.*, 1921, 153R.

[32] *J. Min. Agric.*, Sept., 1921; *J.*, 1921, 371R.

[33] F. Bainbridge, *Iron and Steel Inst.*, *Carnegie Schol. Mem.*, 1920; *J.*, 1921, 124A. See also *Trans. Faraday Soc.*, 1920, **16**, 302; *J.*, 1921, 156A.

[34] G. Scott Robertson, *Trans. Faraday Soc.*, 1920, **16**, 291; *J.*, 1921, 156A.

500 lb. of nitrogen per acre in each of the top and second 9 in. of soil. On ploughing up, the additional fertility of the slagged plots showed itself in increased yields of peas, wheat, and beans.[35] It is not known how this subsequent effect is related to the solubility in citric acid. In view, however, of the rather exiguous nature of the connexion between effectiveness and citric acid solubility it has been again argued that carbon dioxide should be used as solvent instead of citric acid in assessing the value of phosphatic fertilisers.[36]

Ground mineral phosphates are much used in the United States, and there seems some reason to expect that they will come into use in this country also. Present supplies come mainly from the United States and from North Africa[37]; important deposits appear also to exist in Palestine.[38] Much discussion has gone on in this country in regard to Nauru phosphate, extended analyses of which have been published.[39]

Further, a phosphatic guano containing 29·5% P_2O_5 has been found on Latham Island, near Zanzibar.[40] Various other deposits have been recorded. Hitherto the mineral phosphate has been either treated with sulphuric acid to convert it into superphosphate or ground finely and applied direct to the land. Investigators continue to seek for other methods of rendering the phosphate soluble, one of the favourite devices being the use of micro-organisms. In some experiments the rock phosphate is mixed with plant residues, in the hope that the acids produced during the decay of organic matter will attack and dissolve the phosphate. Several investigators, however, have shown that no increase of solubility occurs under these conditions, and it is now suggested[41] in explanation that the bases liberated during the decomposition fully neutralise the acids and prevent their action on rock phosphate. In presence of soil different results may be obtained because soil has the capacity for absorbing basic material. It is also suggested that the addition of sulphur to the mixture would increase its acidity and thus facilitate the solution of phosphate.[42] As the oxidation is largely biological it is considered desirable to ensure the presence of the necessary micro-organisms; this is done by inoculation.[43] One of the most surprising results, if it is substanti-

[35] A. W. Oldershaw, *J. Agric. Sci.*, 1921, **11**, 287; *J.*, 1921, 743A.

[36] H. Hackl, *Chem.-Zeit.*, 1921, **45**, 730; *J.*, 1921, 632A.

[37] See *J.*, 1921, 194R.

[38] W. Packard, *J.*, 1921, 288R.

[39] T. Steel, *J.*, 1921, 59T, 178T.

[40] *Bull. Imp. Inst.*, 1920, **18**, 2; *J.*, 1921, 90R.

[41] F. C. Bauer, *Soil Sci.*, 1921, **12**, 21; *J.*, 1921, 861A.

[42] W. E. Tottingham and E. B. Hart, *Soil Sci.*, 1921, **11**, 49; *J.*, 1921, 232A.

[43] W. H. Martin, *Soil Sci.*, 1921, **11**, 75—86. J. G. Lipman, A. W. Blair, and C. S. Beckwith, *ibid.*, **11**, 87; *J.*, 1921, 232A.

ated, is said to be obtained with yeast, when a high degree of action resulted.[44] Less sensational, but probably no less useful, results are obtained by heating or calcining the rock phosphate.[45] The so-called Rhenania phosphate is made by heating low-grade mineral phosphate rich in carbonate with phonolith, a potassium double silicate. It is claimed that the potash becomes available and that the phosphate becomes equivalent to that in basic slag.[46]

Potassic Fertilisers.

Prior to the war the whole of the potash supply of the world came from Germany, but during the war other sources were opened up. Some of these have not survived the searching test of peace conditions, and it remains to be seen how long the others will last. Germany still retains the largest deposits; it is estimated that for every ton of soluble potash salts in the United States there are 10 tons in France and 6000 tons in Germany, while the estimated productive capacities are[47]:—Germany, 3,850,000 tons; France, 250,000 tons; United States, 80,000 short tons (K_2O).

The German deposits are situated in Central Germany; 86% of the workable potash lies at a depth of some 1200 metres, a further 10% at 1500 metres; deposits below 1700 metres are not worked. In 1920 the pre-war level of output was almost reached, but sales had fallen from 5·2 million tons in 1913 to 4·3 million tons in 1920, the export trade being particularly affected.[48] The Alsace deposits, however, are of great importance and definitely serve to break the German monopoly. The Alsatian mines cover an area of 180 sq. km. and could supply the world requirements for 300 years at pre-war consumption, while Germany with 1500 sq. km. and 200 pits could supply the world for 7500 years. For ease of extraction, however, the advantage is claimed for Alsace.[49] The mines are much more extensively developed than before the war. In 1913 the exports from Alsace were only 40,721 tons K_2O; in 1920 they were 199,175 tons K_2O, of which nearly 18,000 came to the United Kingdom.

The production of potassium salts in the United States has been shrinking; in 1919 there were produced 110,243 short tons (28% K_2O) compared with 207,686 tons in 1918. West Nebraska

[44] M. H. Jacquier, *La Renaissance Agricole*, Oct. 9, 1921.

[45] W. H. Waggaman and T. B. Turley, *Chem. and Met. Eng.*, 1920, **23**, 1057; *J.*, 1921, 77A. Calcining with $CaCO_3$ and sulphurous gases, &c.: J. J. Morel, E.P. 160,847; *J.*, 1921, 402A.

[46] T. Renny and F. Weiske, *Landw. Jahrb.*, 1921, **56**, 1.

[47] *J.*, 1921, 369R.

[48] *J.*, 1921, 351R, 152R; *Z. angew. Chem.*, Feb. 11, 1921; also *J.*, 1921, 53R.

[49] C. Matignon, *J.*, 1921, 407R.

alkali lakes were the chief source, the output from the alunite deposits of Utah and silicate rocks of Wyoming and from kelp being much diminished.[50] There still remain possibilities in America, however; it is said that large deposits have been discovered near Floresville, Texas.[51]

A method of volumetric estimation is based on precipitation as bitartrate.[52]

Some of the American potassic minerals contain boron, probably in sufficient quantity to do injury, especially in a dry season,[53] though it is understood that steps are now taken to remove most of these substances.

In Italy leucite, a double silicate of potassium and aluminium, containing 21·5% K_2O, is used extensively as a fertiliser, and has given excellent results with rice, potatoes, sugar beet, tobacco, rye, oats, and barley. It occurs as a deposit of about 3 sq. km. near Civita Castellana in the province of Rome.[54]

In Norway potash is now being recovered as a by-product from cement kilns. About 2–4 lb. of K_2O is volatilised for each barrel of cement (380 lb.), and in the settled dust it exists mainly as sulphate, but it is not entirely extractable by water owing to the presence of gypsum, with which it forms a sparingly soluble double salt. It is possible to effect considerable separation of potash prior to leaching, since its particles are, on the whole, finer than those of the rest of the dust.[55]

Organic Manures.

Very considerable attention has been devoted to the preparation of artificial farmyard manure. The large increase in arable area brought about by the war at one time seemed likely to result in a glut of straw which could not be profitably utilised in agricultural industry. Experiments have been going on at Rothamsted for some time with the view to making a nitrogenous and humus-forming manure from straw by bacterial decomposition alone. Thorough rotting of the straw is necessary; the conditions to secure this are:—

1. *Air supply.*—Typical rotting occurs only under aërobic conditions. If air is excluded the straw remains unchanged for six months at least.

2. *Supply of soluble nitrogen compounds in suitable concentrations.*—The concentration of even the weakest undiluted urine is above

[50] U.S. Geol. Surv., Dec. 8, 1920; *J.*, 1921, 49R.

[51] *J.*, 1921, 149R.

[52] G. Ajon, *Giorn. Chim. Ind. Appl.*, 1920, **2**, 422; *J.*, 1921, 21A.

[53] J. E. Breckenridge, *J. Ind. Eng. Chem.*, 1921, **13**, 324; *J.*, 1921, 443A.

[54] *U.S. Com. Rept.*, June 1, 1921; *J.*, 1921, 313R; also see G. de Angelis d'Ossat, *Atti R. Accad. Lincei*, 1921, **30**, 379; *J.*, 1921, 710A.

[55] C. Krarup, *Chem. and Met. Eng.*, 1921, **25**, 316; *J.*, 1921, 696A.

the maximum limit for decomposition. No rotting occurs until the concentration of ammonium carbonate has been sufficiently reduced by volatilisation.

3. *Temperature.*—The most rapid changes occur at about 35° C.

If soluble nitrogen compounds are supplied at the rate of 0·73 part of nitrogen per 100 parts of dry straw, all the added nitrogen is converted from a soluble to an insoluble organic form. Rotting will proceed until about 50% of the dry matter has been lost. Little or no loss of nitrogen occurs, so that the final product contains about 2·0% calculated on the dry matter. If soluble nitrogen compounds are added in excess of the limit, loss takes place until the concentration is reduced to the necessary extent, when the action proceeds normally.[56]

It is shown also by experiments at Wainfleet Camp that straw can be used for purifying sewage and there seems little doubt that the resulting product is a useful fertiliser.[57]

Further investigations have been made of activated sludge, chiefly, however, with the view of simplifying the manufacture[58] or of ascertaining the degree of biological purification effected.[59]

The possibility of preparing a merchantable manure from peat continues to attract attention. Two proposals may be mentioned: in one the peat is mixed with 5% of cyanamide and 5–20% of calcium carbonate; potassium salts are also added.[60] In the other peat is treated with distillers' wash or other material rich in sugar and bacteria, and these are fermented in the expectation that a fertiliser[61] will be obtained.

A further attempt has been made to prepare a fertiliser from waste leather by acid digestion.[62]

Sodium and Magnesium Salts as Fertilisers.

The problem is frequently investigated whether and to what extent sodium and magnesium salts can act as fertilisers, and the results often show that crop increases are obtained by their use. Much depends, however, on circumstances. Further instances are recorded where sodium replaces potassium to some extent as

[56] H. B. Hutchinson and E. H. Richards, *J. Min. Agric.*, 1921, **28**, 398.

[57] E. H. Richards and M. G. Weekes, Inst. Civil Eng., June 29, 1921; *J.*, 1921, 559A.

[58] J. Haworth, Inst. Civil Eng., June 29, 1921; *J.*, 1921, 559A.

[59] P. Courmont, *Comptes rend.*, 1921, **172**, 1696; **173**, 181; *J.*, 1921, 559A, 600A.

[60] The Molassine Co. and H. C. S. de Whalley, E.P. 152,779; *J.*, 1921, 21A.

[61] R. B. Goldschmidt and M. Migeon, E.P. 162,738; *J.*, 1921, 481A.

[62] H. Devos, E.P. 147,798; *J.*, 1921, 233A.

food for cereals, and is then found in the leaves and stalks[63]; also, where magnesium sulphate added to a complete fertiliser (nitrogen compounds, calcium phosphate, and sulphate of potash) increased the yield of potatoes.[64]

Some fear has arisen lest the ratio CaO/MgO should be too much disturbed by additions of magnesium salts to soil as fertiliser; it is said that there is some evidence for ratios of 1 : 1 or 1 : 2 according to the nature of the soil, but pot experiments may give misleading results in unskilful hands owing to the crowding of plants, interference of root growth, etc.[65] Examination of the plant ash indicates that the ratio of MgO/CaO is greater than 1 only in the case of sugar beet, maize, potatoes, and mangolds; it equals 1 in wheat and is just under 1 in oats, rye, barley, and buckwheat. The ratios K_2O : MgO : CaO are also discussed.[66]

Fertiliser Analysis.

A number of recommendations have been made by the Association of Official Agricultural Chemists which, however, do not readily lend themselves to summary description; reference must therefore be made to the Journal of that body.[67]

Carbon Dioxide as Fertiliser.

The experiments of Horace Brown and of F. Escombe[68] showed that additions of carbon dioxide to the atmosphere increased assimilation in the leaf, but the plant as a whole was unable to respond and consequently no increase in growth took place. The experiment was repeated by E. Demoussy,[69] who obtained wholly different results; the plant responded and made greater growth when grown in an atmosphere enriched with carbon dioxide. He attributed his success to the circumstance that, unlike Brown and Escombe, he had used no acid in the preparation of his carbon dioxide, and he concluded that part of the function of farmyard manure, green manure, etc., is to increase the supply of carbon dioxide, and thus increase plant growth. This particular deduction is now controverted. Lemmermann could find no evidence that carbon dioxide from dung or green manure was of advantage to the plant. The rate of production of carbon dioxide he maintains is so slow that the composition of the air is not appreciably

[63] T. Pfeiffer, A. Rippel, and C. Pfotenhauer, *J. Landw.*, 1920, **68**, 255; *J.*, 1921, 92A.

[64] A. Jacob, *Z. angew. Chem.*, 1920, **33**, 292; *J.*, 1921, 21A.

[65] O. Loew, *J. Landw.*, 1920, **68**, 225; *J.*, 1921, 92A.

[66] H. Lagatu, *Comptes rend.*, 1921, **172**, 129; *J.*, 1921, 124A.

[67] *J. Assoc. Off. Agric. Chem.*, 1921, Vol. 4.

[68] *Proc. Roy. Soc.*, 1902, **70**, 397.

[69] *Comptes rend.*, 1903, **136**, 325; 1904, **138**, 291; **139**, 883.

affected.[70] Evidence is, however, being brought forward by German chemists to show that plant growth can be increased on the practical side by supplying carbon dioxide up to 0·15% or even 0·2% of the volume of the atmosphere, and some of the data presented are startling. They are summarised by Bornemann[71] up to 1920 and only the subsequent developments need be mentioned here.

Bornemann[72] himself finds that plants grown in frames treated with carbon dioxide for 10 hrs. daily showed increases of 40% or more—especially peas, potatoes, oats, and onions. Unlike Lemmermann, however, he thinks that the increased fertility of dunged soil may in part be due to carbon dioxide evolved therefrom.

The results of F. Riedel[73] have been widely quoted and on them is based a patent which is being exploited in this country. Tho results, it must be admitted, are not very numerous or very satisfying from the practical point of view. They were carried out in a glasshouse 25 metres long and 6 metres wide, and the carbon dioxide was introduced through a double set of pipes pierced with holes which ran the length of the house. Autumn turnips showed considerable increase, and in the seven weeks from August 1st to September 20th yielded on the best plots no less than 20 tons per acre (5 kg. per sq. m.). The interesting feature of Riedel's work is that he uses gases from furnaces removing the carbon dioxide in the first instance by absorption in sodium carbonate solutions from which it is regenerated by use of waste heat. Exception has been taken to the method on the grounds that carbon dioxide so impure as that generated in the Riedel apparatus cannot be relied upon to give increased yields. Claussen[74] has shown that gains in crop yield follow only when pure CO_2 is used. Riedel, however, maintains his position and he has now[75] carried his experiments out of the glasshouse into the open, delivering the carbon dioxide to the growing crop by means of perforated cement pipes; he claims in this way to have obtained yields 1·5 to 3 times that of the control plots, though it is difficult to see how an adequate control could be maintained in the open air The investigation has, however, attracted so much attention from practical growers that the proposed method will probably be tested in this country.[76]

[70] *J.*, 1921, 711A.

[71] F. Bornemann, "Kohlensäure & Pflanzenwachstum": Parey, Berlin, 1920.

[72] *Mitt. deut. Landw. Ges.*, 1920; *J.*, 1921, 711A.

[73] *Stahl und Eisen*, 1919, **40**, 1497; *Mollers Deuts. Gärtner Ztg.*, July 20 and 30, 1921, where some illustrations are given.

[74] *Chem.-Zeit.*, 1920, **44**, 585, 808.

[75] *Chem.-Zeit.*, 1921, **45**, 157.

[76] For a useful summary see R. Cerighelli, *Ann. Sci. Agron.*, 1921, **38**.

Soils.

Soil analysis is probably one of the most unsatisfactory duties a consulting chemist is called upon to perform. It is easy enough of course to obtain figures, but most difficult to interpret them, and often impossible to give the client the information he is entitled to have. From a rather wide personal experience and examination of numerous reports made by professional analysts, the writer is forced to the conclusion that soil analysis on our present knowledge can be used only for comparing similar and comparable soils and not for advising on any particular soil. If one soil has a known agricultural history and can serve as a standard, another soil which is strictly comparable can be tolerably well compared with it after both are analysed. But little or no useful information can be obtained from the examination of a single soil.

Admitting that the purpose of soil analysis is comparison with a standard soil, it falls into two parts. Mechanical analysis enables the physical constitution of the soil to be examined. The coarser portions are easily estimated; for the clay, however, the usual British method is very tedious; Beam's method has been re-examined and is shown to be equally reliable and much more rapid. The differences lie mainly in the use of taller sedimenting vessels and the substitution of 0·05% sodium carbonate for the usual ammonia solution; further, a centrifuge is used instead of the slow sedimentation.[77]

On the chemical side it seems necessary to determine certain bases and certain acids. The most important bases are calcium and potassium, but considerable controversy has arisen as to the proper way of extraction. There is yet nothing approaching agreement, but something is being done to show the condition in which the bases exist in the soil, and ultimately with more precise knowledge it should be possible to find a way out of our present tangle of empirical methods. A paper by Hissink deserves mention. He recognises that bases occur in soils in two widely different forms: (1) Adsorbed, probably as ions, and easily replaceable by other ions, *e.g.*, by treatment with ammonium salts. (2) In a form not so replaceable but yet soluble in acids. It is presumed that the adsorbed bases form the supply immediately available for plant nutrition. Methods are suggested for estimating these: the calcium and magnesium by displacement with $N/1$ sodium chloride, and the potassium and sodium by use of $N/1$ ammonium chloride.

From the point of view of soil analysis importance is attached to the "state of saturation" of the soil, *i.e.*, the ratio of the number of adsorbed cations to the number which the soil is capable of

[77] A. F. Joseph and F. J. Martin, *J. Agric Sci*, 1921, **11**, 293; *J.*, 1921, 743A.

adsorbing; but there is as yet no accurate method for determining the latter.[78]

Investigations such as these[79] will no doubt afford a basis for the development of a true scientific method, but in the meantime the problem is being attacked empirically; pot experiments are set up with different soils; these are examined by the help of a number of different solvents, and that one is finally selected which gives results most in accordance with the crop yields. Lemmermann and his colleagues[80] have done some of the best of this work and have shown that their method of relative solubilities (for potash: proportion of total which is soluble in 10% hydrochloric acid, and for P_2O_5: proportion of total which is soluble in 1% citric acid) helps to account for the observed behaviour of fertilisers in soils, though they do not agree that any method of chemical analysis can *a priori* determine the fertiliser requirements of soil.

In the Texas experiments[81] $N/5$ nitric acid was considered the most suitable reagent, although care is necessary in interpreting the results as soils differ in their ease of yielding up phosphates to the plant, even when they contain the same quantity of soluble phosphate: *e.g.*, surface soils give up more than subsoils of equal content, and non-acid soils more than acid soils. Yet another method which has accorded well with pot experiments is to autoclave the soil and extract the potash with water.[82] No solvent, however, can give absolute figures: much depends on the conditions. Some attention has been devoted to the influence of soil reaction. The absorption of phosphorus by plants is affected by the reaction of the soil, though to a different extent for different crops. Maize could absorb difficultly-soluble phosphates in acid soil only; addition of lime reduced the amount absorbed. Mustard, on the other hand, was able to absorb the same phosphate in more alkaline solution. The ratio of $CaO : P_2O_5$ absorbed was in maize 3 : 1 and in mustard 15 : 1. This ratio measures the capability of the plant to utilise P_2O_5 and to induce change in reaction. The cations are preferentially absorbed early, thus leaving a reaction favourable to assimilation of phosphate.[83] It is further claimed that the ratio potash : lime is important; any considerable increase in the supply of lime brings about a repression of potash assimilation

[78] D. J. Hissink, *Versl. Landbouwk. Onderzoek. Rykslandbouwproefstat.*, 1920, 144; *J.*, 1921, 359A.

[79] See also L. Casale, *Staz. Sper. Agrar. Ital.*, 1921, **54**, 65; *J.*, 1921, 710A.

[80] O. Lemmermann, L. Fresenius, and H. Wiessmann, *Landw. Versuchs-Stat.*, 1921, **98**, 155; *J.*, 1921, 820A.

[81] G. S. Fraps, *Texas Agric. Expt. Sta. Bull.*, 267, 1920; *J.*, 1921, 820A. See also O. M. Shedd, *Soil Sci.*, 1921, **11**, 111; *J.*, 1921, 232A.

[82] J. König and J. Hausenbäumer, *Landw. Jahrb.*, 1920; a good résumé of investigations carried out during the past 20 years.

[83] M. Wrangell, *Landw. Versuchs-Stat.*, 1920, **96**, 209; *J.*, 1921, 54A.

which may result in considerable injury, which can, however, be remedied by heavy dressings of potassic fertilisers.[84]

Soil Reaction.

This important factor is being closely studied and it is hoped that useful and easily-worked methods will soon be available. A résumé of the whole subject was published early in the year by E. A. Fisher,[85] but other methods have been subsequently described,[86] and the whole subject is rapidly advancing.

[84] P. Ehrenberg, *Landw. Jahrb.*, 1920, **14**, 1.

[85] *J. Agric. Sci.*, 1921, **11**, 19, 45; *J.*, 1921, 231A.

[86] *E.g.*, L. Michaelis and A. Gyemant, *Biochem. Zeits.*, 1920, **109**, 165; *J.*, 1921, 102A. O. Lemmermann and L. Fresenius, *J. Landw.*, 1921, **69**, 97; *J.*, 1921, 555A.

SUGARS, STARCHES, AND GUMS.

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Sugars.

Statistics published by Willett and Gray,[1] for the year ending October 27, 1921, give the world's production of sugar as 16,555,059 tons, comprising 11,831,715 tons of cane sugar and 4,723,344 tons of beet sugar. The figure for cane sugar is only about 70,000 tons below that for the previous year, but most producing countries showed a small increase, the joint effect of which is offset by a decrease of 700,000 tons in India. European beet production showed an increase of about 1,125,000 tons over the yield of the 1919-20 campaign, and the present campaign is expected to show a further increase of about 200,000 tons. Estimates for the production of cane sugar for the year 1921-22 are, of course, only tentative, but in most countries a decrease is expected, amounting in the aggregate to about 1,000,000 tons.

The outstanding feature of the present year for the sugar industry has been the fall in prices, which, starting from an unprecedented height in 1920, have probably not yet reached bottom. The chief factor responsible for raising prices to a pinnacle two years ago appears to have been the expectation that the world's consumption would rapidly tend to attain pre-war dimensions and also that in consequence of the prohibition of alcoholic beverages in the United States, the consumption of sugar in that country would increase enormously. These expectations have not been realised, and in view of the impoverished condition of Europe it seems probable that European consumption will recover very slowly. It is true that the world's production of sugar (cane and beet) is some two million tons less than just before the war, but during that period the production of cane sugar, stimulated by conditions due to the war, has increased by about two million tons. This means that the production of beet sugar is about four million tons less than before the war. Unless the cane sugar industry can supply sugar at a price which will prevent the full recovery of the beet industry,

[1] *Int. Sugar J.*, 1921, **23**, 653.

it will be faced with a very difficult situation until the world's consumption of sugar has recovered to something like the pre-war level. The difficulty will be felt most keenly by factories erected during or since the war at a great outlay of capital. In Cuba, where a vast amount of capital has been sunk within recent years during the reign of high prices, the fall in prices produced acute financial difficulties, resulting in a moratorium, for much of the plant is not yet paid for; and in the early part of the year 1921 a Sugar Commission was appointed by the Cuban Government to control the price of sugar for export.

In the United Kingdom the past year has seen the official demise of the Royal Commission on the Sugar Supply appointed in August 1914. Its operations are described in a series of annual Reports, the last of which (to March, 1921) contains some general observations on State trading. In the course of its seven-years' life it made purchases of sugar amounting to more than 9 million tons.

Cane Sugar.

Manufacture.—In three-roller cane mills the pressure between the top roller and the rear one is required to be much greater than between the top and front rollers, and for mills of this type having a movably mounted top roller, F. J. de Bruin[2] claims a form of construction in which the hydraulic pressure acting on the top roller is directed more towards the rear than towards the front roller, so as to ensure adequate compression of the cane in the rear gap. The direction in which the hydraulic pressure acts on the top roller can be adjusted, within certain limits, by various alternative means. A further form of construction is also claimed[3] in which hydraulic pressure is applied to the rear as well as the top roller, the front one being fixed. This arrangement remedies certain disadvantages associated with other types, in which the forcing apart of the front and top rollers by irregular charging results in a lessening of the pressure in the rear gap also. By the new construction the hydraulic pressure on the rear roller ensures constancy of pressure on the cane in the rear gap even when the top roller is lifted. In mills with two rollers (or under certain conditions in those with more than two), C. McNeil[4] provides means for adjusting the relative positions of the upper and lower rollers in a direction at right angles to the plane containing the axes of the two rollers, for which purpose the housings of the upper roller make contact with those of the lower roller over guiding surfaces which permit a sliding motion in the direction named.

[2] E.P. 162,533; *J.*, 1921, 444A.
[3] E.P. 149,289; *J.*, 1921, 633A.
[4] E.P. 161,726.

It has been mentioned in previous Reports[5] that the intensive milling of the cane which has been practised within recent years, notably in Hawaii, has certain disadvantages, viz., the juice as a whole has a lower quotient of purity than juice obtained by the older milling plants, and also it is liable to contain abnormal amounts of fine suspended matter, or *bagacillo*, which is difficult to eliminate. With regard to the latter point, S. S. Peck[6] suggests that a considerable improvement could be realised by the use of fine juice-strainers of 100-mesh instead of the comparatively coarse strainers usually employed. A further point in connexion with these recent milling processes is raised by J. N. S. Williams,[7] who suggests that appreciable losses of sugar by inversion are likely to occur as the result of fine shredding and extreme crushing of the cane and maceration with filter-press washings and thin juices from the last unit. As evidence that such losses do occur he cites some comparative data for several factories; these data show a higher value for the calculated sucrose in the cane for factories practising moderate crushing and maceration but working an inferior cane, than for factories working a superior cane but with extreme crushing and compound maceration, although the percentage extraction was greater in the latter than in the former cases. Such losses of sugar during milling would not be revealed by the usual methods of factory control, for a direct accurate determination of the sugar in the cane is impracticable, and the indirect method employed is based on the sum of the sugar in the juice and that in the bagasse. As the percentage extraction is calculated on this indirect estimate it does not necessarily represent the proportion of the sugar originally present in the cane which has been extracted. Some experiments recorded by G. Loos and A. Schweizer[8] are of interest as bearing on this question of sugar losses during milling. In these experiments it was found that whilst the sugar-content of very finely divided bagasse diminished from 3% to nil in 7 hours, the deterioration was much slower in bagasse less finely divided and largely freed from rind by screening. The observed deterioration is attributed by the authors to the action of enzymes present in the rind of the cane. M. Bird[9] describes attempts made to minimise fermentative processes during milling operations in a factory in British Guiana. A small proportion of milk of lime together with some commercial formaldehyde (2 pints of the latter daily) was allowed to flow in a thin continuous stream into the juice leaving the last unit of the milling train, and this juice was employed

[5] *Ann. Repts.*, 1918, 365.
[6] *Int. Sugar J.*, 1921, **23**, 158; *J.*, 1921, 271A.
[7] *Ibid.*, 1921, **23**, 271; *J.*, 1921, 443A.
[8] *Arch. Suikerind. Ned. Indië*, 1921, **29**, 21; *J.*, 1921, 670A.
[9] *La. Planter*, 1921, **66**, 184; *J.*, 1921, 670A.

for macerating the bagasse from the first unit. The results were so satisfactory that the proportion of lime used was increased, and ultimately the whole of the lime required for the defecation of the factory juices was added in this way. This method of operating is now in use in several factories with very satisfactory results, as it assists clarification, facilitates the attainment of the correct reaction for defecation, and relieves the filter presses to some extent owing to a portion of the impurities precipitated by the lime being retained in the bagasse.

Difficulties encountered in an Egyptian sugar factory, in the defecation of certain raw juices from sound canes, are attributed by C. Muller[10] to the liberation of colloidal organic substances containing silicic acid from the plant cells in the milling of the cane. These substances are not precipitated by lime, but if the juice is superheated at 116° C. before liming the organic component is coagulated and the silica is precipitable by lime. This treatment is stated also to improve the colour of the juice, to reduce the amount of lime required for defecation to one-third of the usual amount, and to enable sulphitation to be omitted or postponed until the juice has been evaporated to syrup.

Recent apparatus for the separation of suspended matters from raw or defecated sugar juices shows no sign of becoming standardised in type at present, for the patents published during the period under review embody a number of widely different principles. In an apparatus claimed by J. Miller and G. Fletcher and Co.,[11] the juice is forced upwards through a layer of bagasse held between horizontal perforated plates in a vessel supported pivotally on hollow trunnions which also serve to conduct the juice to and from the vessel. The trunnions are connected by a yoke passing above the vessel and carrying a screw for fixing a cover on the vessel and for compressing the layer of bagasse to any required extent in the course of filtration. Apparatus patented by C. G. Petree[12] for the continuous treatment of defecated juice is of the conical type with a discharge outlet for deposited sludge at the bottom, an inverted weir device at the top for collecting floating matter and a gallery and helical baffle plate to control the flow of juice through the apparatus. An intermittent-acting juice filter in which a piston-like filtering medium is forced downwards through the juice in a closed vessel is claimed by F. Tiemann.[13] E. C. Carrick[14] has patented a straining apparatus of an entirely different type in which the filtering surface forms the periphery of a cylindrical

[10] *Bull. Assoc. Chim. Sucr.*, 1921, **20**, 239; *J.*, 1921, 402A.

[11] E.P. 158,387 and 161,993; *J.*, 1921, 203A, 421A.

[12] E.P. 162,206; *J.*, 1921, 444A.

[13] E.P. 161,987; *J.*, 1921, 633A.

[14] U.S.P. 1,367,946; *J.*, 1921, 272A.

vessel rotating about a horizontal axis and divided into radial compartments in which a partial vacuum is maintained while they are in the upper part of their travel. The juice to be strained is fed on to the upper part of the revolving vessel, the liquid is drawn into the underlying compartments, the solids retained on the filtering surface are removed therefrom by a scraper at a later stage of the revolution of the vessel, and still later the internal compartments arriving at the lowest part of their travel discharge their liquid contents through the filtering surface into a trough below the apparatus. E. G. Aizcove[15] proposes to allow defecated juice to travel slowly along a closed-in channel with upwardly sloping floor, and to incorporate this device as part of an evaporating unit, the vapour space bring situated at the inlet end of the channel, whilst the calandria is situated at the other end and supplied with clarified juice through the channel. Centrifugal separators for defecated juice are claimed by F. W. Fischlein[16] and by W. Mauss.[17] The former apparatus contains a series of conical screens mounted on a rotating shaft within a closed casing, whilst in the apparatus claimed by Mauss the suspended matters in the juice are thrown against the imperforate walls of a rotating chamber consisting of separable sections.

The hypothesis advanced by A. Schweizer[18] to account for certain hitherto unexplained losses of sugar in factory working in Java, which was referred to somewhat sceptically in last year's Report, must apparently now be regarded as untenable. Schweizer's theory was that sucrose was inverted and even further decomposed by the "atomisation" of syrup particles in the evaporating plant. W. D. Helderman and C. Sijlmans[19] have since carried out experiments in which hot sucrose solutions were repeatedly converted into spray, but they found no evidence of any appreciable amount of inversion of the sugar. On the other hand, J. S. de Haan's conclusion that the losses referred to are due to entrainment of the juice in the evaporating plant is confirmed by obervations of W. C. Nieboer[20] who reports that as the result of the installation of two spray-separators of the whirling blade type in place of juice-catchers of the Hodek type in a Javan factory, the unexplained sugar losses have been reduced from 4·07% to 2·65%, which represents a saving of about 152 tons of white sugar on a crop of 10,768 tons.

Much interest continues to be manifested in the subject of the presence of fine sugar grain in final molasses. It will be remem-

[15] U.S.P. 1,358,132; *J.*, 1921, 22A.

[16] E.P. 161,822; *J.*, 1921, 402A.

[17] E.P. 164,418; *J.*, 1921, 535A.

[18] *Ann. Repts.*, 1920, **5**, 396.

[19] *Arch. Suikerind. Ned. Indië*, 1921, **29**, 495; *J.*, 1921, 596A.

[20] *Ibid.*, 1920, **28**, 1889; *Int. Sugar J.*, 1921, **23**, 646.

bered that a few years ago H. Kalshoven[21] investigated many samples of molasses in Java and concluded that they contained on the average 8% of fine sugar crystals and some contained as much as 17–18%. E. O. von Lippmann[22] subsequently found quantities up to 13% in beet molasses. Some doubt has been thrown upon the accuracy of these figures, for the method employed by Kalshoven for determining the sugar grain has been criticised from several sides. This method is based on the comparison of the refractometric dry-substance content of the original molasses with that of the sample diluted with water in order to dissolve the sugar crystals present, the latter value being of course calculated back to the undiluted molasses. A similar method had been employed by Stanek and Skola for determining the purity of the syrups in massecuites without removing the grain, but according to J. Dedek[23] the method was found to be subject to so many sources of error that it had to be abandoned. The determination depends, in fact, upon a small difference between two refractometric readings which are liable to considerable uncertainty. The use of water for diluting also involves errors, as pointed out by J. Tischtschenko.[24] For example, Dedek found that when the method was applied to a beet molasses entirely free from microscopic crystals an amount of fine grain was indicated which varied according to the degree of dilution; when the sample was diluted with 21·4% of water it appeared to contain 1·18% of grain, but when diluted with 97·3% of water 4·89% of sugar grain was indicated. In view of these considerations Dedek recommends that dilution should be avoided altogether, by taking the second reading on a portion of the sample which has been heated in a firmly closed metal container for ¼ hr. at about 110° C. in a bath of glycerin and shaken at intervals to dissolve any crystals present. Operating in this way on a number of beet molasses, Dedek found amounts of raw grain ranging from nil to 18.7%, the average being 6·9%. Kalshoven's method indicated much larger amounts, for example 18% instead of 13% in one case. A. Schweizer has expressed doubts whether such large proportions of sugar grain can actually be present in molasses. He found that when a molasses which had been filtered through thick cloth was mixed with 3–5% of finest sugar dust it had the appearance of an opaque mass having somewhat the character of massecuite, and even 2% of fine sugar could be detected on spreading the molasses on a glass plate. Moreover, he failed to detect any evidence of sedimentation in molasses kept for a long time in tanks, the upper and lower layers having practically the same

[21] *Ann. Repts.*, 1919, **4**, 384.

[22] *Z. Ver. deuts. Zukerind.*, 1919, **44**, 527; *J.*, 1920, 420A.

[23] *Listy Cukrovarnicke*; *Int. Sugar J.*, 1921, **23**, 327; *J.*, 1921, 523A.

[24] *Z. Ver. deuts. Zuckerind.*, 1909, 103; *J.*, 1909, 253.

composition after long storage. The subject would thus appear to require further study, particularly as regards the validity and limits of error of the refractometric method employed to determine the sugar grain. Some experiments carried on in a Javan factory by W. D. Helderman[25] appear to show that large quantities of recoverable sugar may be lost in molasses. A low-grade massecuite cooled in the usual way, in unlagged tanks, yielded 22% of sugar on centrifuging, but by leaving the massecuite to cool very slowly in insulated tanks for two months, and then centrifuging, the yield of sugar was increased to 28–31%, the crystals were larger and more regular in shape than those obtained by the former treatment, and the resulting molasses was quite free from grain.

Deterioration of Raw Sugars.

N. Kopeloff, H. Z. E. Perkins, and C. J. Welcome[26] have made a study of the changes occurring in a large number of bags of raw Cuban sugar, of different marks and qualities, in the course of storage for eight weeks in a warehouse in New Orleans under ordinary storage conditions. The original polarisation of the various sugars ranged from 92 to 98, the moisture-ratio[27] (*i.e.*, W/(100–S) where W and S are the percentages of water and sucrose respectively) ranged from 0·18 to 0·50 and the number of micro-organisms per gram of sugar ranged from 67 to 134,000. Chemical and bacteriological tests carried out after four and eight weeks' storage showed that most of the sugars had undergone appreciable deterioration, that is, a fall in polarisation, amounting in some cases to more than 1%, usually accompanied by an increase in reducing sugar. There was a decided increase also in the number of micro-organisms, which could be correlated with the degree of deterioration within certain limits. In general the number of micro-organisms per gram of sugar was greater at the centre than at the surface of the bags, doubtless because the atmospheric conditions (average temperature 67° F., relative humidity 81) were such that the outer layers of sugar tended as a rule to become drier during storage. A study of the results indicates that neither the "moisture-ratio," nor the number of micro-organisms per gram is by itself a satisfactory criterion of the liability of a sugar to deterioration; of the two factors mentioned, considered singly, the second is more to be relied upon than the first, for whilst predictions based on the number of organisms proved wrong in 33 cases out of 141, predictions based on the moisture-ratio were falsified in 86 cases out of 141. By taking both factors into account more valid generalisations can be made, but these are subject to

[25] *Arch. Suikerind. Ned.-Indië*, 1921, **29**, 694; *J.*, 1921, 784A.

[26] *J. Agric. Res.*, 1921, **20**, 637; *J.*, 1921, 271A.

[27] *Ann. Repts.*, 1919, **4**, 385.

exceptions. Samples having any moisture-ratio common in raw Cuban sugars (0·2–0·5) are practically certain to deteriorate during storage if they contain more than 50,000 organisms per gram. If the number of organisms does not exceed 500 the danger of deterioration is much less in the case of sugars having moisture-ratios below 0·36, but there is ample evidence to show that even if the moisture ratio is reduced below 0·3, which is considered the critical point, deterioration may take place in sugars containing more than 200 micro-organisms per gram. It has been shown that the use of superheated steam in the centrifuges will reduce the number of organisms in a sugar by more than 90%, so that by this means the danger of deterioration may be practically eliminated provided the factor of safety or moisture ratio is also properly controlled. Certain moulds of the genera *Penicillium* and *Aspergillus* are regarded by W. J. T. Amons [28] and by P. A. van der Bijl [29] as among the most active agents causing deterioration in sugar, and various species isolated from sugar are described by both these investigators. Van der Bijl considers that bacteria, as distinct from moulds, only play an important part in excessively moist sugars. In order to produce sugars not liable to undergo change during storage, he suggests that from the boiling of the massecuite onwards all factory operations should be carried out under aseptic conditions as far as possible, that plant and utensils should be disinfected periodically, and that the sugar should be dried before being bagged.

A method proposed by D. Grant [30] for preventing or minimising deterioration in raw sugars intended for refining, is to mix with the sugar a small proportion, for example 0·5–6%, of dry finely powdered decolorising carbon or other adsorbent material such as kieselguhr. The added material by adsorbing moisture present in the sugar, renders the latter much drier to the touch and much less liable to deterioration during storage and transport. A particular advantage claimed for this treatment is that the sugar is rendered sufficiently dry and crumbly to be shipped in bulk and conveyed by pneumatic transport, like grain. The treatment of the raw sugar by this process is stated to facilitate and effect economies in refining, but of course it would necessitate that the refiner's methods must be adapted to deal with sugar treated in this way.

Decolorising Carbons.

Several patented processes for the preparation of these products have been published during the past year. De Bruyn, Ltd. and

[28] *Arch. Suikerind. Ned.-Indië*, 1921, **29**, 1; *J.*, 1921, 670A.
[29] *Int. Sugar J.*, 1921, **23**, 504; *J.*, 1921, 745A.
[30] E.P. 159,640; *J.*, 1921, 362A.

C. Revis[31] employ as raw material the filter press residues from the refining of edible oils such as cottonseed oil. M. B. Punnett and R. A. Whitaker[32] impregnate sawdust or other vegetable material with a concentrated solution of a sulphate, such as nitre-cake, and carbonise at 300–500° C. in open retorts in presence of air, after which the product is leached, dried, powdered, and reheated at 800°–1000° C. in absence of air. In a process claimed by C. S. Hudson[33] sawdust, corn-cobs, or other suitable material is impregnated with about twice its weight of phosphoric or boric acid and carbonised below a red heat, but preferably above 375° C. The yield of decolorising carbon obtained is stated to amount to 90% of the amount of carbon contained in the raw material and its decolorising action on raw sugar solutions is five times as great as that of the best decolorising carbons hitherto available. The phosphoric or boric acid is leached out and employed repeatedly. The decolorising power of the product varies according to the proportion used and the temperature of carbonisation. Between 300° and 375° C. a soft carbon is obtained which possesses only moderate decolorising power, whilst between 400° and 600° C. a hard and very active product is obtained suitable for industrial use. The high yield and exceptional activity of the product claimed for this process are attributed to the use of an acid capable of forming esters with the carbonaceous materials whereby the course of carbonisation is profoundly modified, and further the presence of the hot acid flux maintains the surface of the particles of carbon clean and prevents oxidation.

In a suggestive paper by E. G. R. Ardagh[34] a *resumé* is given of the present state of our knowledge concerning the conditions favourable to the production of active decolorising carbons. The conditions mentioned are (1) the use of organic material rich in silica, lime, or nitrogenous substances, (2) impregnation of the material with inorganic salts or oxides, that remain solid or volatilise at the temperature of carbonisation, or impregnation with nitrogenous substances such as casein, (3) high temperatures and prolonged heating, (4) in certain cases the action of steam or carbon dioxide at a certain optimal temperature, (5) extraction of the mineral impregnating agent after carbonisation, and (6) reduction of the product to a fine powder. Experiments on fine sawdust from hard maple wood confirm these conclusions. When the sawdust was carbonised in an atmosphere of nitrogen at 850° C. the adsorbent capacity of the product for caramel increased with the duration of carbonisation. Previous impregnation of the sawdust

[31] E.P. 162,117; *J.*, 1921, 426A.
[32] U.S.P. 1,383,755; *J.*, 1921, 618A.
[33] E.P. 139,156; *J.*, 1921, 426A.
[34] *J.*, 1921, 230T.

with suitable inorganic salts improved the product, the best results being obtained by impregnating with ammonium magnesium chloride or by mixing the sawdust with an equal quantity of calcium phosphate. Whether the sawdust was impregnated or not, however, the decolorising power of the product was invariably increased by extracting with hydrochloric acid.

In the same paper an account is given of the theoretical conclusions reached by N. K. Chaney [35] in his work on the preparation of active carbon for gas masks, which was carried out for the United States Chemical War Service. Chaney distinguishes two forms of amorphous carbon: one, the α-form, possesses great adsorbent power and is readily attacked by oxidising agents, whilst the other, or β-form, is inactive and more resistant to oxidation. In general the α-form is produced by the chemical or thermal decomposition of carbonaceous material at temperatures below 500°–600° C., whilst the inactive form is produced at temperatures above 800° C. In the destructive distillation of organic matter at low temperatures the α-carbon produced adsorbs hydrocarbons and the product obtained under such conditions, which is designated "primary carbon," is a very stable complex of hydrocarbons adsorbed on a base of active carbon. Many animal and vegetable carbons consist of "primary carbon" and so also do cokes prepared from bituminous coal at low temperatures. "Secondary carbon" is "primary carbon" which has been partially or completely broken down with the formation or introduction of inactive carbon by the high-temperature carbonisation of hydrocarbons forming part of the primary carbon itself or derived from extraneous matters. The problem of producing active carbon, according to this view, consists in selecting or producing a primary carbon and then by differential oxidation or distillation removing the adsorbed hydrocarbons from the base of α-carbon. The beneficial effect of impregnating agents is due to their action in removing these adsorbed hydrocarbons. They also undoubtedly render the carbon more porous, but Chaney distinguishes adsorbent power due to porosity, or "capillary capacity," from the "specific capacity" which is a characteristic of α-carbon. In relation to the adsorption of gases capillary capacity is fundamentally different from specific capacity. It is characterised by the rapid attainment of equilibrium, that is, gases at high concentrations are rapidly absorbed, but also rapidly released when the concentration is reduced. Specific capacity, on the other hand, is characterised by the power of adsorbing gases at low concentrations, and by great retentivity. These theoretical views deserve consideration inasmuch as they suggested several methods of preparing active carbons which proved successful.

[35] *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 91; *J.*, 1919, 857A.

The comparison of the decolorising power of samples of carbon and the choice of a satisfactory numerical constant to express the results have engaged the attention of A. B. Bradley and F. E. Thomas. The problem is one of considerable difficulty, for the effect produced by a sample depends on factors which have not yet been fully elucidated. Very useful work in this direction has been done by Bradley[36] in an investigation of the action of a number of decolorising carbons on a 50% solution of a raw Jamaican sugar under similar conditions, the liquid being treated with 5% of the decolorising carbon, heated just to boiling, filtered by suction on a Buchner funnel, and examined with a Lovibond tintometer to determine the percentage of colour removed. From these comparative tests it is concluded (1) that in general the carbons which possess the lowest decolorising power also give rise to the slowest filtrations, (2) that the percentage of carbon in the samples is not a measure of the decolorising power, (3) that the relative decolorising efficiencies of a number of samples may vary according to the concentration of the sugar solution employed, (4) that the presence of a large proportion of very fine particles, passing through sieves of mesh higher than 84, is detrimental in respect of decolorising action and rate of filtration, and (5) that the decolorising and filtering efficiencies of a sample depend on its bulk or porosity, as measured by the volume occupied by 5 g. of the sample. Bradley is inclined to regard the last-mentioned factor as of chief importance in determining decolorising power, but the size of the particles also plays a part. Carbons containing a large proportion of very fine grain become rapidly exhausted on continued use, whilst those containing the largest proportion of medium-sized grain, say those passing a sieve of 84-mesh but retained by one of 106-mesh, maintain their activity longest. F. E. Thomas[37] emphasises the practical importance of expressing the decolorising power of carbons in such a way as to indicate the relative amounts of the samples required to produce equal decolorising effects, and he proposes to adopt "Norit" as standard, and to test other samples by ascertaining the percentages of the latter necessary to produce the same decolorising effect as 5% of "Norit" on a raw sugar solution of 50° Brix under certain standard conditions, the percentages being in all cases referred to the sugar present. In a later paper Bradley[38] criticises certain of Thomas's suggestions and urges that a satisfactory comparison of decolorising power cannot be based on the behaviour of the standard carbon at one concentration only, for the relative efficiencies of different carbons vary according as larger or smaller proportions of all are used. In view of the im-

[36] *Int. Sugar J.*, 1921, **23**, 25; *J.*, 1921, 157A.
[37] *Ibid.*, 1921, **23**, 162; *J.*, 1921, 271A.
[38] *Ibid.*, 1921, **23**, 455; *J.*, 1921, 671A.

portance of the bulk or porosity of the samples and the size of the grains, these factors also should be taken into account in any scheme of standard tests. The main points in the scheme suggested by Bradley are as follows: (1) The adoption of a standard tintometer, preferably that of Hess-Ives, (2) the use of a 50% raw sugar solution for the tests, (3) the adoption of a standard carbon of the highest decolorising power, such as "Super-Filtchar," (4) the determination of the percentages of colour removed by various proportions, ranging from 1 to 6%, of the standard carbon and also of the samples under examination, so that graphs may be plotted to exhibit the relative efficiencies at different concentrations, (5) the observation of the times required for the filtration of a given volume of the treated solutions, under standard conditions, (6) the determination of the proportions of the samples capable of passing through screens of different mesh, for example 60, 106, and 124, and (7) the determination of the volume of a given weight of the samples, as a measure of porosity and also of friability. It is to be hoped that the publication of the papers referred to above will lead to an exchange of views between chemists concerned with the manufacture and use of decolorising carbons in the sugar industry, for as the number of carbons on the market increases and their use becomes more general, satisfactory methods of valuation adapted to the requirements of the different branches of the sugar industry will become urgently necessary.

It is well known that decolorising carbons are more effective in acid than in neutral or alkaline solutions, and in an investigation with raw cane juices J. F. Brewster and W. G. Raines[39] have confirmed this fact in terms of hydrogen ion concentration. It was found that the concentration of hydrogen ions in normal cane juices is in the neighbourhood of the value $p_H=5$, but it varies considerably in different cases and not always in the same direction as the acidity determined by titration. For example, one juice, 10 c.c. of which required 1·43 c.c. of $N/10$ alkali for neutralisation had a p_H value of 4·8, whilst another requiring 2·0 c.c. of alkali had a lower hydrion concentration, viz., $p_H=5{\cdot}0$. It was found that the decolorising effect of a carbon on raw juice increases with increase in the concentration of hydrogen ions, but in view of the fact that decolorisation is usually carried out on the hot juice, it is not considered advisable to work with a hydrion concentration exceeding $p_H=5$, the natural reaction of the juice, owing to danger of inversion of sucrose. J. N. A. Sauer[40] claims that the advantages of working with an acid liquid can be realised without actual acidification, by employing a decolorising carbon which has been boiled with excess of acid, washed until the washings are neutral, and

[39] *J. Ind. Eng. Chem.*, 1921, **13**, 1043; *J.*, 1921, 863A.
[40] E.P. 166,229; *J.*, 1921, 633A.

not subsequently dried. The moist carbon thus treated retains adsorbed acid and acts on sugar solutions as if the latter were acid. Sauer[41] has also patented a process for the systematic treatment of sugar liquors with decolorising carbons, the main feature of which is that batches of the liquid at different stages of decolorisation are passed in turn, the lightest first and so on, through the same charge of carbon in a filter press, or in the case of the first and last batches of liquid the carbon may be mixed with the liquid and transferred to the presses with the latter. The General Norit Company[42] claim a process and apparatus for the treatment of liquids with decolorising carbon, in horizontal mixing cylinders fitted with agitator blades and each with an internal filter fitted in front of the liquor outlet at the top of the chamber, to retain particles carried away by the liquid and to return them to the body of the chamber.

Beet Sugar.

British Beet Sugar.—The Kelham beet sugar factory was opened on November 2, 1921, and is now in operation. It is owned by Home Grown Sugar, Ltd., with a capital of £700,000, part of which, as stated in a previous Report,[43] has been guaranteed by the British Government. The factory has been designed and the greater part of the machinery supplied by a French firm and the operations are under French supervision. It has a capacity of 600 tons of beets per day of 24 hours, and its output for a campaign is 8000 tons of sugar, 3000 tons of dried beet pulp, and 1800 tons of molasses. On the first year's working it is certain to make a heavy loss, for it is paying £4 a ton for roots, which will involve the expenditure of £19,000 more than the price obtainable for the sugar produced, and to this loss must be added all the manufacturing costs. The large capital which has been required owing to the high cost of erecting and equipping such a factory at the present time, will unfortunately continue to be a heavy burden even when the prices of beets, materials, and labour have found their economic level, but the experiment will be watched with great interest, and if it succeeds there should be no difficulty in securing capital for later enterprises of a similar kind when the costs of building and equipment have become more favourable to success than they have been in this case.

Manufacture of Beet Sugar.

In a series of studies of the carbonatation process, V. Stanek has investigated several points of practical interest which deserve

[41] E.P. 155,600; *J.*, 1921, 361A.
[42] E.P. 163,505; *J.*, 1921, 456A.
[43] *Ann. Repts.*, 1919, 4, 390.

notice. By stirring the juice for about half an hour at 85° C. after the first carbonatation, instead of filtering it immediately, the quotient of purity of the juice was found to be appreciably improved; for example, with one juice a purity of 94·1% was obtained, as compared with 93·3% by immediate filtration, and no detrimental effect was produced on the colour, alkalinity, or salt-content of the juice.[44] The calcium salts of organic acids present in the juice or produced by decomposition of invert sugar, are not completely eliminated by carbonatation, and in order to obtain a clarified juice as free from calcium salts as possible, Stanek[45] proposes to treat the juice, preferably before the completion of carbonatation, with a small quantity of sodium carbonate or sulphite equivalent in amount to the calcium salts of organic acids present. In the ordinary carbonatation process calcium sulphate present in the juice is removed much more completely than corresponds with its solubility in the juice[46]; this is possibly due to adsorption by the precipitated calcium carbonate or to the formation of insoluble double compounds with the latter. The effect of the carbonatation process on the amino-acids present in beet juice has also been investigated by Stanek.[47] Solutions containing 0·1% of asparagine, aspartic acid, glutamic acid, or leucine, together with 15% of sucrose, were treated with 2% of lime at 85° C. and subjected to carbonatation. This treatment removed 62% of the aspartic acid, 40% of the glutamic acid, 16% of the asparagine, and 6% of the leucine from solution, and by using 4% of lime instead of 2% still larger proportions of the amino-acids were precipitated, for example 80% of the aspartic acid. By treating the filtered juice from the first carbonatation with 0·2% of lime and again saturating further amounts of the amino-acids were removed, viz., aspartic acid 14%, glutamic acid 7%, asparagine 2%, and leucine 0·1%, but much better results were obtained by substituting sulphitation for the second carbonatation, viz., aspartic acid 24%, glutamic acid 11%, asparagine 3%, and leucine 2%. Thus the removal of aspartic and glutamic acids is throughout more complete than that of asparagine and leucine. In order to eliminate asparagine as completely as possible from raw beet juice, therefore, it must be converted into aspartic acid, for which purpose prolonged contact of the juice with lime before saturation is advantageous. In a further communication[48] the same author recommends a triple carbonatation for the treatment of juices from frozen or altered beets, which are liable to contain abnormally large amounts of invert sugar.

[44] *Z. Zuckerind. Böhm.*, 1918, **42**, 417; *J.*, 1920, 126A.
[45] *Z. Zuckerind. Czechoslov.*, 1919, **44**, 45, 53; *J.*, 1920, 379A.
[46] *Ibid.*, 1921, **46**, 1; *J.*, 1921, 783A.
[47] *Z. Zuckerind. Czechoslov.*, 1921, **45**, 45; *J.*, 1921, 863A.
[48] *Ibid.*, 1920, **45**, 53; *J.*, 1921, 190A.

Beyersdorfer [49] draws attention to the danger of destruction of sucrose associated with the practice of using the sweet water from the filter presses for the slaking of the lime employed for clarification; owing to the heat developed on slaking, as much as 5–15% or even more of the sucrose in the sweet water may be decomposed, the chief products being acetic and lactic acids, which, of course, increase the calcium content of the carbonated juice.

In the filtration of carbonatation sludge in the usual presses, coarse particles tend to sink to the bottom of the filter chambers, and consequently the lower portion of the sludge cakes are more porous than the upper portion, and in washing the cakes the water passes more readily through this porous region than through the upper part, so that the sugar is removed unequally. To remedy this, A. Müller [50] proposes to retard the flow of water through the lower part of the cakes by various alternative means, for example by employing extra thick filter cloths in the lower part of the press or by reducing the size of the perforations in the lower part of the metal plates.

The possibility of recovering some of the ammonia liberated from beet juice in the course of raw sugar manufacture is discussed by several authors. Donath [51] has suggested that in a factory slicing 6000 quintals (600 metric tons) of beets daily as much as 383 kg. of ammonium sulphate could be recovered per day from the clarification department alone. This estimate is shown by subsequent investigators to be many times too high. From experiments in a beet sugar factory, K. Andrlik and V. Skola [52] estimate that the amount of ammonia liberated during carbonatation represents about 0·0019% of the weight of beets sliced, a further 0·0058% is evolved during the subsequent heating of the juice, and 0·0074% is found in the condensed water drained from the multiple effect evaporators. In a practical trial it was found that the ammonia actually recoverable from the waste gases from the carbonatation amounted only to about 0·00075% of the beets, and Silhavy [53] arrived at a very similar estimate, viz., 0·00073% corresponding to 4·38 kg. of ammonia or 16·9 kg. of ammonium sulphate per 6000 quintals of roots sliced; whilst J. Hrada [54] found that still smaller proportions, viz., 0·0002–0·0005%, were evolved from limed juice maintained at 80°–90° C. for 30–50 mins. It seems clear, therefore, that under practical conditions very little ammonia can be recovered from the juice during clarification; much larger

[49] *Z. Ver. deuts. Zuckerind.*, 1921, 75; *J.*, 1921, 233A.

[50] G.P. 332,579; *J.*, 1921, 597A.

[51] *Z. Zuckerind. Czechoslov.*, 1919, **44**, 61; *J.*, 1920, 379A.

[52] *Ibid.*, 1921, **45**, 179, 187, 195; *J.*, 1921, 315A.

[53] *Ibid.*, 1921, **45**, 155; *J.*, 1921, 233A.

[54] *Ibid.*, 1921, **45**, 156.

amounts are liberated during the subsequent heating and evaporation of the juice, but their economical recovery is a problem which has not yet been solved.

In the boiling of massecuites from syrups of high purity, such as first-product beet syrup, M. von Wierusz-Kowalski[55] proposes to centrifuge the massecuite hot after only a portion, for example 40%, of the sugar has crystallised, and to subject the separated syrup to sulphitation before boiling further to grain. Owing to the lowering of the quotient of purity of the syrup, due to the separation of part of the sugar, sulphitation can be used with greater advantage since it may be carried farther than would be safe with the original syrup. E. Mozer[56] claims a process and apparatus for the draining of massecuites in the vacuum pan, especially suitable in cases where the sugar is to be remelted at once. The vacuum pan has a screened outlet at the bottom for the molasses, and also means for introducing syrup or water for the cleansing or redissolving of the sugar.

A reference to the subject of fine grain in beet molasses will be found above in the paragraphs dealing with cane molasses. A comparative study of the Steffen lime process, the strontia process, and a similar one involving the use of baryta, for the desacharification of beet molasses has been carried out by M. Potvliet.[57] The precipitated saccharate was in each case filtered, pressed, washed with a solution of the respective alkaline-earth, and decomposed by means of carbon dioxide. The washing involved loss of sugar in all cases, especially in the strontia process. The solution of the recovered sugar obtained after filtration of the carbonatation sludge from the strontia process was light straw yellow in colour, that from the baryta process was slightly darker, whilst the juice from the Steffen process was very much darker, the relative colour values being 2·25, 2·92, and 8·60 respectively. The original molasses contained 48·5% of sucrose, and the yields of sugar obtained were: 35·45% by lime, 43·18% by strontia, and 43·97% by baryta, and in the last two cases no trace of the respective alkaline-earth metals could be detected in the sugars. It is concluded that, apart from the cost of materials, the strontia and baryta processes are more convenient and efficient than the Steffen lime process. The mother liquors from the two former processes can be concentrated to 42° B. without difficulty, and they then contain at least 12% of potash and 4% of nitrogen. Two new processes for rendering beet molasses edible may be briefly mentioned. In one proposed by H. C. Cutler[58] the molasses is heated with hydrochloric acid to invert a part of

[55] E.P. 137,849; *J.*, 1921, 597A.
[56] G.P. 339,109; *J.*, 1921, 745A.
[57] *J. Ind. Eng. Chem.*, 1921, **13**, 1041; *J.*, 1921, 864A.
[58] E.P. 169,113; *J.*, 1921, 785A.

the sucrose present and then subjected to dialysis in order to remove the acid and the greater part of the salts present, after which it is boiled, filtered, and evaporated to the required consistency. The second process, patented by W. D. Bonner,[59] consists in treating the diluted molasses with tartaric acid to remove potash, evaporating the filtered liquid to eliminate its unpleasant flavour, and treating the separated tartar with sulphuric acid to recover tartaric acid for further use, and potassium sulphate.

MISCELLANEOUS.

Sucrose.—J. Reilly [60] has investigated the products obtained by heating sucrose under reduced pressure. It appears that under these conditions some *l*-glucosan is formed, a result of interest in view of the fact that this compound is obtained from cellulose, starch, and dextrin by similar treatment.[61] The amount of *l*-glucosan obtained from sucrose, however, is very small as compared with that obtained from cellulose etc. Since, according to the views of Pictet and Karrer,[62] the *l*-glucosan obtained in these decompositions is derived from β-glucose groups, it would seem that, provided the decompositions of sucrose and cellulose follow similar lines, the β-glucose structure is not present as a main grouping in the sucrose molecule.

Lactose.—J. Gillis [63] has determined the solubility of lactose in water at various temperatures and finds that it ranges from 34·9% by weight of anhydrous lactose in the solution at 57·1° C. to 86·7% at 178·8° C. M. Bridel [64] finds that emulsin hydrolyses lactose in alcoholic solution to dextrose and galactose, the latter being converted into ethyl-β-galactoside. J. Tavroges, J. W. Roche, and G. Martin[65] claim a process of manufacture in which whey is freed from lactalbumin by means of a suitable colloid prior to recovery of the lactose; thus the whey is heated to 70°–80° C. and treated with sodium thiosulphate, the negatively charged colloidal sulphur thus precipitated throwing down the positively charged albumin.

Galactose.—E. P. Clark [66] prepares this sugar by boiling a solution of lactose in 2½ times its weight of 2% sulphuric acid for 2 hours, the solution then being neutralised with barium carbonate, decanted through decolorising carbon and concentrated under reduced pressure until its weight is 1·1 times that of the lactose taken.

[59] U.S.P. 1,362,078; *J.*, 1921, 93A.
[60] *J.*, 1921, 249T.
[61] *Ann. Repts.*, 1918, **3**, 126.
[62] *Ann. Repts.*, 1920, **5**, 135.
[63] *Rec. Trav. Chim.*, 1920, **39**, 677; *J.*, 1920, 829A.
[64] *Comptes rend.*, 1921, **173**, 501; *J.*, 1921, 745A.
[65] E.P. 161,887; *J.*, 1921, 403A.
[66] *J. Biol. Chem.*, 1921, **47**, 1; *J.*, 1921, 596A.

The warm syrup is treated with ethyl and methyl alcohols and seeded and left to crystallise. The crude sugar may be purified by acidifying a 25% aqueous solution with acetic acid, concentrating and treating with 95% alcohol.

Mannose.—P. M. Horton[67] prepares this sugar from ivory nut shavings by a process in which the powdered material is first treated with sodium hydroxide and then hydrolysed with sulphuric acid; a yield of about 23% of fairly pure mannose is obtained.

Rhamnose.—C. F. Walton, jun.,[68] employs "Lemon Flavin," which is rich in quercetrin, for preparing rhamnose. The flavin is hydrolysed by boiling for 30 min. with 10 parts of 0·5% sulphuric acid, and the solution, filtered from the residue of quercetin, is neutralised with barium carbonate, decolorised, concentrated under reduced pressure to a solid-content of about 40%, treated with 3 vols. of warm absolute alcohol, filtered and concentrated to a solid-content of 70–80%; the rhamnose crystallises on cooling the solution and may be recrystallised from 80% alcohol. A 20–25% yield is obtained.

Analysis of Sugar-Products.

There is perhaps no branch of chemical analysis which presents more difficult problems than those encountered in the case of mixtures of several sugars or of sugars and other carbohydrates. The classic methods dependent on optical activity and reducing power before and after hydrolysis or fermentation are quite satisfactory in many cases, but in others they do not give complete and accurate data. The schemes of analysis, based on these methods, for the analysis of mixtures, though satisfactory for two or three constituents, generally involve such an accumulation of errors that the figures obtained for the remaining constituents are very untrustworthy. During the last few years, however, much progress has been made in the discovery and development of methods for the determination of individual sugars; moreover, since some of these methods depend on principles or reactions altogether different from those involved in the older methods, the results obtained by the former methods serve as useful checks on those obtained by the latter. As will be seen from what follows, a great advance has been made in this direction in the past year.

Optical Methods.

V. Stanek[69] confirms the observation of Bates and Jackson[70] that the Herzfeld-Schönrock value, 34·657, for the $[\alpha]_D^{20}$ of a sucrose

[67] *J. Ind. Eng. Chem.*, 1921, **13**, 1040; *J.*, 1921, 864A.

[68] *J. Amer. Chem. Soc.*, 1921, **43**, 127; *J.*, 1921, 272A.

[69] *Z. Zuckerind. Czechoslov.*, 1921, **45**, 417; *J.*, 1921, 711A.

[70] *Ann. Repts.*, 1917, **2**, 392.

solution polarising 100° Ventzke is too high. Bates and Jackson obtained the value, 34·620, and Stanek's work would appear to show that the value is still lower. In view of the extreme importance of this factor, further revision with a view to obtaining an agreed figure is certainly necessary.

The proposal to adopt a new normal saccharimetric weight of 20 g. put forward by C. A. Browne[71] and others is opposed by a large majority of British chemists[72] on the grounds that the inconvenience, expense, and confusion caused by the change would outweigh any advantages. Further, the 26·00 g. normal weight adopted by the International Commission for Uniform Methods of Sugar Analysis in 1900, insures greater accuracy of observation than can be attained with the smaller weight proposed.

The work of Jackson and Gillis[73] on the determination of sucrose by the method of double polarisation and on the value of the Clerget divisor has been the subject of controversy between these workers[74] and C. A. Browne[75]; it is doubtful if the last word has been written on the subject, and the questions must be left in dispute for the present. From the work of Jackson and Gillis,[76] O. Schrefeld,[77] and Browne and Gamble,[78] it appears that the Clerget divisor, 132·66 at 20°C., which is valid under the Herzfeld conditions of sucrose inversion, becomes 133·0 under the Jackson-Gillis conditions of inversion. Browne and Gamble point out that the adoption of the latter divisor involves alteration in the formulæ used in the analysis of mixtures of sucrose and raffinose. The percentages of sucrose, S, and raffinose, R, are found from the formulæ

$$S = \frac{0{\cdot}514\ P - P^1}{0{\cdot}844}; \qquad R = \frac{0{\cdot}33\ P + P^1}{1{\cdot}563}$$

P and P^1 being the direct and invert polarisations at 20°C.

V. Sazavsky[79] recommends the use of a 6% solution of tannin followed by basic lead acetate solution for clarifying raw beet products, and states that although commercial tannin is optically active, it is completely precipitated by basic lead acetate and thus introduces no error. It is said that solutions so treated require no further clarification after inversion. H. T. Kalshoven

[71] *Ann. Repts.*, 1919, **4**, 396.
[72] *J.*, 1921, 120R.
[73] *Ann. Repts.*, 1920, **5**, 413.
[74] *Int. Sugar J.*, 1921, **23**, 217, 445; *J.*, 1921, 361A, 671A.
[75] *Ibid.*, 1921, **23**, 166, 276, 516; *J.*, 1921, 271A, 443A, 745A.
[76] *loc. cit.*
[77] *Z. Ver. deuts. Zuckerind.*, 1920, 409; *J.*, 1921, 157A.
[78] *J. Ind. Eng. Chem.*, 1921, **13**, 793; *J.*, 1921, 821A.
[79] *Z. Zuckerind. Czechoslov.*, 1921, **45**, 227; *J.*, 1921, 443A.

and C. Sijlmans[80] find that clarification with basic lead nitrate, followed by aluminium sulphate, is preferable to the use of basic lead acetate for Java cane molasses.

According to J. Badreau[81] the rotatory power of mannitol is increased by arsenious acid especially in alkaline solution, and since the sugars in general are not affected by this reagent, mannitol, in admixture with sugars, may be determined by a process of double polarisation.

Copper Reduction Methods.

Herzfeld's well-known gravimetric method for determining small proportions of invert sugar in presence of sucrose by means of Fehling's solution cannot be used when the proportion of invert sugar is less than 0·05%. A sample of sucrose containing 0·05% of invert sugar yields 50 mg. of copper under the Herzfeld conditions, and sucrose freed as completely as possible from invert sugar yields 20 to 40 mg. of copper. The need of a more delicate method has been felt by all who have had occasion to purify sucrose, either for standardisation or for bacteriological purposes, and several methods of copper reduction designed for determining extremely small proportions of invert sugar have been described in recent years.[82] Of these the latest is that due to A. Kraisy,[83] who uses a much more dilute solution than that of Fehling, and replaces the sodium hydroxide of the latter by sodium carbonate; the amount of copper reduced is found by determining the excess iodometrically. Kraisy found that whereas 10 g. of purified sucrose yielded 36–43 mg. of copper from Fehling's solution, it gave only 1·5–4·6 mg. by his method, and he concludes that it is thus possible to detect as little as 0·002% of reducing sugar in refined sugar.

It is a well known fact that in the clarification of sugar juices with basic lead acetate a certain proportion of the reducing sugars is precipitated, and the solution, freed from excess of lead with sodium oxalate, carbonate, or chloride, is found to contain less reducing sugar than the original juice. According to J. B. Harris,[84] if the excess of lead is removed by adding oxalic acid to the liquid containing the lead precipitate, the acid decomposes the insoluble compound of lead and reducing sugars, and the clarified solution contains the whole of the reducing sugars originally present.

[80] *Arch. Suikerind. Nederl.-Indië*, 1921, **29**, 989; *J.*, 1921, 863A; *cf.* Deorr, *J.*, 1915, 503.

[81] *J. Pharm. Chim.*, 1921, **24**, 12; *J.*, 1921, 597.

[82] *Cf.* Pellet, *Ann. Repts.*, 1917, **2**, 398; Beyersdorfer, *Ann. Repts.*, 1920, **5**, 415; Bates, *ibid.*

[83] *Z. Ver. deuts. Zuckerind.*, 1921, 123; *J.*, 1921, 315A.

[84] *J. Ind. Eng. Chem.*, 1921, **13**, 925; *J.*, 1921, 783A.

It has long been known that Barfoed's solution may be used for detecting monoses in presence of lactose or maltose, since, under certain conditions, it reduces the former but not the latter sugars. Attempts to employ this reagent quantitatively have not been very successful in the past, but according to L. Le Grand,[85] it gives accurate results under the following conditions :— 5 c.c. of the sugar solution, containing not more than 0·1 g. of sugar, is boiled with 15 c.c. of Barfoed's solution for 3 minutes in a conical flask. The amount of cuprous oxide obtained is a measure of the amount of hexose ; and if the total reducing sugars are determined with Fehling's solution, the amount of lactose or maltose is found by difference. The method should prove a most useful aid in the analysis of complex mixtures of sugars.

C. A. Browne[86] proposes an expeditious method for converting the cuprous oxide obtained in gravimetric determinations of reducing sugars to metal ; the crucible containing the oxide is heated to dull redness and plunged into the vapour of methyl alcohol.

Iodometric Method.[87]

This method for estimating aldose sugars, which depends on the oxidation of the sugar to the corresponding monocarboxylic acid, has been much investigated during the past few years, but it is only recently that the degree of accuracy attainable has been fully explored by H. M. Judd[88] and by J. L. Baker and H. F. E. Hulton.[89] The procedure adopted by these chemists consists in treating a solution of 0·1 g. of the sugar in 10 c.c. of water with 20 c.c. of $N/10$ iodine, and then with 30 c.c. of $N/10$ sodium hydroxide, the mixture being allowed to stand for 3–5 minutes, after which it is acidified with sulphuric acid and the excess of iodine titrated with $N/10$ thiosulphate. The reaction is not strictly quantitative, and carbohydrates other than aldoses show "iodine absorptions" which must be taken into account in analysing mixtures of aldoses and other sugars. Baker and Hulton have determined the weights of iodine equivalent to 1 g. of the more important sugars under the prescribed conditions. Although the method is limited in its application to commercial products, owing to the fact that organic non-sugar substances absorb iodine in some cases, it is of considerable utility in the examination of products such as

[85] *Comptes rend.*, 1921, **172**, 602 ; *J.*, 1921, 272A. *Ann. Falsif.*, 1921, **14**, 132, 264 ; *J.*, 1921, 555A, 783A.

[86] *J. Assoc. Off. Agric. Chem.*, 1919, **3**, 261 ; *J.*, 1920, 829A.

[87] *Ann. Repts.*, 1917, **2**, 394.

[88] *Biochem. J.*, 1920, **14**, 255 ; *J.*, 1920, 668A.

[89] *Ibid.*, 1920, **14**, 754 ; *J.*, 1921, 361A.

honey, which contain a large proportion of aldose, and of mixtures of pure or nearly pure sugars.

Miscellaneous.

G. Van B. Gilmour [90] proposes to utilise the observation that lævulose combines with boric acid to form a stronger acid, for the estimation of this sugar in invert sugar etc., a weighed quantity of the sample in $M/10$ boric acid solution being titrated with $N/10$ sodium hydroxide. Gilmour gives figures showing the relation between quantities of lævulose and volumes of alkali solution. The method appears to mark an entirely new departure in sugar analysis, and, like the iodometric method for aldoses, it may prove a useful aid in the analysis of complex mixtures of sugars.

A. Jonescu and V. Vargolici [91] recommend alkaline ferricyanide solution for determining reducing sugars. Thus, 10 c.c. of a solution containing 46 g. each of potassium ferricyanide and potassium hydroxide is diluted with 20 c.c. of water and heated to boiling, the sugar solution being added until decolorisation occurs. If the sugar solution is coloured, 10 drops of 1% picric acid are added as indicator. Ten c.c. of the ferricyanide solution is equivalent to 10 c.c. of 0·5% dextrose solution.

Bruhns [92] points out that artificial honeys prepared by the acid hydrolysis of sucrose contain dextrinous substances which are only partially hydrolysed under Clerget conditions, so that the total solids often amount to 3–5% more than the sum of the reducing sugar and "sucrose" found by the Clerget method. If, however, a 1% solution of the honey in 0·06N hydrochloric acid is heated in a boiling water-bath the dextrinous substances are completely hydrolysed in the course of a few hours, and if the heating is continued until the maximum reducing power is attained and a correction is made for the destruction of lævulose during heating, the reducing sugar content so obtained agrees to within 0·5% of the total solid content. Bruhns also observes that partial hydrolysis of honey dextrins in the Clerget process may account for the small amounts of "sucrose" frequently supposed to be present in genuine honeys. Bruhns' opinion is supported by the writers' experience according to which the dextrin isolated from genuine honeys undergoes some decrease in rotatory power when subjected to Clerget hydrolysis. According to Bakker, [93] who used Jolles' method [94] for determining sucrose, honey does not contain more

[90] *Analyst*, 1921, **46**, 3; *J.*, 1921, 125A.

[91] *Bul. Soc. Chim. Romania*, 1920, **2**, 38; *J.*, 1920, 829A.

[92] *Chem.-Zeit.*, 1921, **45**, 661; *J.*, 1921, 633A.

[93] *Rec. Trav. Chim.*, 1921, **40**, 600; *J.*, 1921, 821A.

[94] *J.*, 1910, 1467.

than 1% of sucrose, and it is possible to detect the addition of as little as 2% of sucrose to genuine honey; even if the bees are fed on sucrose, practically the whole of the latter undergoes transformation. This question of sucrose in honey is important since the presence of more than a small proportion is indicative of spurious or adulterated honey. Unfortunately there is some divergence of opinion as to the maximum amount of sucrose in genuine honey, and it seems unlikely that the limit can be fixed so low as that found by Bakker since much evidence of the occurrence of genuine honeys of considerably higher sucrose-content has been adduced. There certainly appears to be reason for further investigation of the question. Genuine honeys which appear to contain more than, say, 1 or 2% of sucrose when tested either polarimetrically or by copper reduction before and after inversion should be tested by Jolles' method or by the iodometric method before and after inversion.

A committee of German chemists and manufacturers [95] of artificial honey has proposed the following with regard to this comestible. Artificial honey must be of good keeping qualities, contain not more than 0·3% of ash, and possess a honey-like aroma. The acids used for inversion must be technically pure and free from substances injurious to health, and the free acidity of the product must not exceed 2 mg. equivalent to 100 g. of honey. The dry substance-content must be at least 78% and the content of unchanged sucrose must not exceed 25%. Starch syrup and starch sugar, provided that they are of good edible quality, may be added to the extent of 20%. The artificial honey must be so prepared as to give Fiehe's reaction strongly; addition of genuine honey for flavouring is permissible. Further, the honey must be vended in correctly labelled packages.

For determining the dry substance in artificial honey, V. Stanek and J. Vondrak [96] recommend (1) the refractometric method applied to the undiluted material previously warmed if necessary to dissolve crystals, or (2) the following method: The sp. gr. of a mixture of the sample with an equal weight of water (in degrees Balling) is corrected for temperature if necessary, and then multiplied by 2, and from the product 0·7° is subtracted to allow for the effect of contraction on dilution.

G. L. Spencer [97] has devised an electric oven for the rapid determination of water in bagasse etc. A current of air, drawn through the oven by a vacuum pump, is first heated by an electrical resistance and then passes into the drying chamber, the bottom of which is provided with an annular channel. The material to be

[95] A. Beythien, *Chem.-Zeit.*, 1921, **45**, 1026.

[96] *Z. Zuckerind. Čzechoslov.*, 1921, **45**, 203; *J.*, 1921, 402A.

[97] U.S.P. 1,348,757; *J. Ind. Eng. Chem.*, 1921, **13**, 70; *J.*, 1921, 191A.

dried is placed in metal capsules, the bottoms of which are made of Monel metal filter cloth. The capsules fit tightly into openings in the channel which is connected with the vacuum pump. With this oven bagasse can be dried in 30 mins. and raw sugar in 10 mins.; whilst according to G. P. Meade[98] the dry substance of honey, syrup, and molasses may be accurately determined by absorbing the diluted (1 : 1) material in fine asbestos and heating for 20 mins. in the oven at 110° C. in a strong current of air. For purposes of factory control the oven should prove extremely useful.

To remove air from molasses in determining the specific gravity of the latter pycnometrically, W. B. Newkirk[99] attaches a bulb, provided with a stopcock, to the pycnometer. The pycnometer having been completely and the bulb partly filled with the molasses, the apparatus is placed under reduced pressure, and when bubbles of air no longer collect in the bulb, the pycnometer is disconnected, stoppered, and weighed.

For the determination of potash, *e.g.*, in molasses, E. Sherrill[100] describes a method according to which the potassium is precipitated as cobaltinitrite in a centrifuge tube; the volume of the precipitate, after centrifuging, is compared with that obtained from a standard solution of potassium chloride under similar conditions.

Starch, Inulin, etc.

Starch.—During the past year a large amount of research has been carried out on the nature of starch, and although there remains a wide divergence of opinion as to the constitution of the starch complex, very great progress has been made. In particular the work of Karrer and his colleagues, referred to below, appears to throw much light on this very difficult problem.

The gelatinisation of starch by caustic alkali is rapid, even at the ordinary temperature, but A. Reychler[101] states that if a solution of alkali hydroxide of about 0·135 mol. per litre concentration is used, gelatinisation is slow enough for convenient observation under the microscope. Acids and some neutral salts in concentrated solution exert a similar action, but sulphates show the reverse effect; thus sodium, ammonium, and magnesium sulphates cause, within a few minutes, complete coagulation of a starch paste which, without such addition, would only be partially coagulated in 10 or 12 days. Courtonne[102] also finds that at the ordinary temperature solutions of certain chlorides convert starch into

[98] *J. Ind. Eng. Chem.*, 1921, **13**, 924; *J.*, 1921, 783A.

[99] *U.S. Bureau of Standards Technol. Paper No.* 161, 1920; *J.*, 1920, 829A.

[100] *J. Ind. Eng. Chem.*, 1921, **13**, 227; *J.*, 1921, 281A.

[101] *Bull. Soc. Chim. Belg.*, 1920, **29**, 118, 309; *J.*, 1921, 402A, 444A.

[102] *Comptes rend.*, 1921, **171**, 1168; *J.*, 1921, 55A; *J.*, 1905, 630.

paste, and at 115° C. convert the latter into soluble starch, a saturated solution of magnesium chloride being the most effective. Reychler's microscopical observations, lead him to support Maquenne's view that starch is composed of the two substances amylocellulose or amylose and amylopectin. Maquenne's theory is also supported by M. Samec and H. Haerdtl[103] who state that starch can be separated by electro-dialysis into a highly viscous and electro-conducting fraction, amylopectin, and a non-viscous and non-conducting fraction, amylose; the proportion between these constituents varies with different starches. The same workers find that all starches contain phosphorus, the amount of which ranges from 0·012% in tapioca to 0·112% in potato starch, and they assign mean molecular weights to various starches which range between the enormously high figures of 77,500 for maize starch to 260,000 for maranta starch. Such values would seem to render the problem of the constitution of starch quite hopeless, but according to Karrer and his colleagues[104] the true starch molecule is by no means so unwieldy. Thus, it is pointed out in the first place that estimates of the molecular weight of starch based on the properties of its colloidal solutions must necessarily be far too high since such solutions are not solutions of individual molecules but of molecular aggregates. To arrive at a true value for the molecular weight it is necessary to prepare starch derivatives which yield true solutions. Karrer and his colleagues have succeeded in this, preparing three methylostarches, of which the most highly methylated, $C_6H_8O_3(OCH_3)_2$, forms a true aqueous solution with a molecular weight of 1200 at most, and it is concluded that the starch molecule contains not more than 6 dextrose residues. The number may well be less, and further work indicates that starch is a polymerised α-diamylose (maltose anhydride). Again, starch resembles the amyloses of Schardinger[105] and Pringsheim[106] (not to be confounded with Maquenne's amylose) in yielding acetobromomaltose when treated with acetyl bromide, and the heats of combustion of starch and these amyloses indicate that whilst α-octoamylose is the highest polymeric form of α-amylose possible, starch is probably a member of a series of products isomeric with the α-amyloses and possibly corresponding with α-tetra-amylose or β-hexa-amylose.

According to H. Tryller,[107] starch is present in the potato in the form of the potassium salt of starch-phosphoric acid; in the process of manufacture, however, the potassium is replaced or partially

[103] *Koll. Chem. Beihefte*, 1920, **12**, 281; *J.*, 1921, 272A.

[104] *Helv. Chim. Acta*, 1920, **3**, 620; 1921, **4**, 169, 185, 263, 678; *J.*, 1920, 795A; 1921, 361A, 784A.

[105] *J.*, 1909, 153; 1911, 439.

[106] Pringsheim and Langhans, *J.*, 1912, 1001; Pringsheim and Eissler, *J.*, 1913, 985.

[107] *Chem.-Zeit.*, 1920, **44**, 833; *J.*, 1920, 829A.

replaced by calcium (and to some extent by magnesium, iron, and manganese) derived from the water used for washing the starch.

E. Herzfeld and R. Klinger[108] propose a method for preparing various polysaccharides from plant tissues which involves preliminary treatment with warm sodium hydroxide solution; it is claimed that this treatment effects the degradation of various impurities to products which are soluble in alcohol. Thus the preparation of starch is as follows: Fresh potato pulp or starch meal made to a paste with water is heated with 33% solution of sodium hydroxide on the water-bath, the alkali being added gradually until the bulk of the material has been converted into a transparent, mucilaginous mass. This is strongly centrifuged to remove insoluble matter, the clear, viscid liquid then being warmed and treated with small quantities of 90% alcohol until no more precipitate is thrown down; the bulk of the proteid matter, lipoids, etc. remains dissolved in the alkaline alcoholic liquor. The precipitate is redissolved and precipitated three times and finally redissolved, neutralised with hydrochloric acid, and precipitated with alcohol. The method is adversely criticised by M. Samec,[109] who states that the alkaline treatment leads to an amylopectin product more or less deficient in amyloses, or to disintegration products unlike the original starch.

According to a process for the manufacture of starch from potatoes claimed by H. Wertheim and Nyitraer Stärke-Industrie-A.-G.,[110] the potato pulp, freed from juice as far as possible, is treated with the minimum amount of water to remove the remaining extractive matter, the starch being finally washed out with water in the usual way. It is stated that the process allows of the complete recovery of all valuable constituents and avoids the difficulties of dealing with waste waters. E. H. Harvey[111] claims a process for modifying starch in which the material is subjected to the action of an electric current in a conducting bath until it has been converted into soluble starch.

H. Lührig[112] finds that in Ewer's polarimetric method for determining starch slight alterations in the concentration of the acid used do not affect the accuracy of the results, but the prescribed time of heating should not be exceeded.

E. Horton[113] finds that the method of determining starch by hydrolysis with taka-diastase is not satisfactory, different preparations of the enzyme from *Aspergillus oryzæ* giving widely divergent

[108] *Biochem. Zeits.*, 1920, **107**, 268; *J.*, 1921, 784A.
[109] *Biochem. Zeits.*, 1921, **113**, 255.
[110] G.P. 331,378; *J.*, 1921, 403A.
[111] U.S.P. 1,366,653; *J.*, 1921, 234A.
[112] *Pharm. Zentralh.*, 1921, **62**, 141; *J.*, 1921, 272A; *J.*, 1908, 238.
[113] *J. Agric. Sci.*, 1921, **11**, 240; *J.*, 1921, 745A.

results. This difficulty may be overcome by making control analyses of pure starch with each preparation of the enzyme before and during the period of its use.

Dextrins.—According to J. C. Blake,[114] erythrodextrin is best prepared from dextrins which are of low amylodextrin-content. The dextrin solution is treated with dilute alcohol to precipitate amylodextrin, and the erythrodextrin is separated as a heavy liquid by adding more alcohol. On treating this liquid with ammonium sulphate, the erythrodextrin separates in a state of high purity.

A recent process proposed by Zellstoff-fabr. Waldhof and V. Hottenroth[115] for the manufacture of sugar and dextrin consists in treating wood or other cellulosic material with sulphuric acid in quantity and of concentration insufficient to dissolve the cellulose. The mixture is allowed to stand for some time, then diluted with water and boiled. Thus, 1 kg. of sawdust requires 1 litre of 75% acid, and after standing some hours 14 litres of water is added; the lignin remains undissolved and the dextrin in the solution is converted into sugar by boiling. The whole of the acid, if the dextrin is required as such, or the excess of acid above that required for converting the dextrin into sugar, is removed by dialysis; or it may be precipitated as calcium sulphate.

Inulin.—In view of the potential economic importance of inulin as a source of alcohol for power purposes, the chemistry of this carbohydrate is of special interest. As long ago as 1867 Dubrunfaut[116] observed that during winter the inulin present in artichoke tubers is transformed into sucrose and an optically inactive, non-crystallisable sugar. Dubrunfaut's observation is partially confirmed by H. Colin,[117] whose experiments lead to the conclusion that during winter part of the inulin in the tuber is transformed into sucrose whilst the remainder undergoes progressive degradation to lævorotatory substances—lævulosans—of less lævorotatory power than inulin. These lævulosans, unlike inulin, are hydrolysed by invertase and fermented by yeast. Phenomena, essentially the same as the above, occur during the winter months in chicory roots. The lævulosans are obviously identical with the inulides described by J. Wolff and B. Geslin.[118] Colin[119] also finds that dextrorotatory carbohydrates, elaborated in the leaves, serve for the synthesis of inulin in the artichoke, this synthesis beginning in the stem and being completed in the tubers; the inulin-content of the fully-grown tuber does not begin to diminish until November.

[114] *J. Amer. Chem. Soc.*, 1920, **42**, 2673; *J.*, 1921, 93A.

[115] G.P. 309,150, 310,149, 310,150, 340,212; *J.*, 1920, 204A; 1921, 866A.

[116] *Comptes rend.*, 1867, **64**, 764.

[117] *Ibid.*, 1918, **166**, 305.

[118] *Ibid.*, 1917, **165**, 651: 1918, **166**, 429; *J.*, 1917, 1286; 1918, 220A.

[119] *Bull. Assoc. Chim. Sucr.*, 1919, **37**, 121; *J.*, 1920, 245A.

One of the most valuable contributions to the chemistry of the carbohydrates for some years is that of J. C. Irvine and E. S. Steele,[120] whose work throws much light on the constitution of inulin. These authors find that inulin $(C_6H_{10}O_5)_x$ can be successively methylated to di- and trimethylinulin; since the latter represents the limit of methylation, it appears that inulin contains three hydroxyl groups in each $C_6H_{10}O_5$ unit. Trimethylinulin, on hydrolysis, yields trimethyl-γ-fructose, and the latter can be converted into tetramethyl-γ-fructose identical with the tetramethylfructose obtained by the hydrolysis of octamethylsucrose. Hence sucrose and inulin are in close structural relationship, and, from the uniformity of the products obtained in the various reactions, it is concluded that inulin is an aggregate of γ-fructose residues, each ketone molecule having lost two hydroxyl groups in the formation of the polysaccharide.

The above conclusions are supported by the observations of E. Bourquelot and M. Bridel[121] on the action of inulase on inulin, and by the work of H. Pringsheim and A. Aronowsky[122] on triacetylinulin.

A. Daniel[123] has patented a process for obtaining inulin and lævulose from plant juices in which the raw material, *e.g.*, dahlia tubers, is heated with strong alkalis, the foreign matter being thereby precipitated or converted into an innocuous form.

[120] *Chem. Soc. Trans.*, 1920, **117**, 1474; *J.*, 1921, 93A.

[121] *Comptes rend.*, 1921, **172**, 946; *J.*, 1921, 402A.

[122] *Ber.*, 1921, **54**, 1281; *J.*, 1921, 523A.

[123] G.P. 313,986; *J.*, 1920, 37A.

FERMENTATION INDUSTRIES.

By ARTHUR SLATOR, PH.D., D.SC., F.I.C.

SEVERAL matters of general interest to the fermentation industries have occurred during the year under review. With the official termination of the war on September 1st a large measure of decontrol of the brewing industry came into effect. Beers no longer have to conform to an arbitrary average gravity, and this relaxation is a very welcome one. It is, however, hardly likely to cause any great increase in the average strength of beers, for the heavy tax of £5 per standard barrel still remains. The stoppage of the supply of coal in the early summer increased the importance of using fuel to its utmost advantage, and favoured the introduction of oil for heating purposes. The Institute of Brewing research scheme includes a systematic investigation of hops, and already some reports on the subject have been published. Timber for cask-making is also receiving attention, and the literature dealing with the evaluation of barley is being collected. A new section of the Institute has been formed at Burton-on-Trent.

An interesting account of the reconstruction of the brewing industry of Northern France is given by E. Boullanger and H. Lloyd Hind.[1] Since the last report was written some important lectures on matters concerning these industries have been delivered. A. Chaston Chapman took as his subject for three Cantor Lectures, "Industrial Micro-biology," and gave a very able account of the technical uses of micro-organisms.

A tribute to the fundamental work and charming personality of the late Prof. Adrian J. Brown is paid by Prof. H. E. Armstrong[2] in a memorial lecture delivered to the Institute of Brewing. Many matters of interest relating to fermentation chemistry are discussed, and although general agreement with all the arguments brought forward is unlikely, there is much in the lecture to stimulate thought and consideration.

CHEMISTRY.

This section of the report deals with the chemistry of enzymes and fermentation.

[1] *J. Inst. Brew.*, 1921, **27**, 54.

[2] *J. Inst. Brew.*, 1921, **27**, 197.

General Enzymes.

Many attempts are being made at the present time to obtain information regarding the constitution of enzymes.

T. Bokorny[3] has investigated the action of nitrous acid on enzyme preparations. Nitrogen is liberated, indicating the presence of amino-groups. From pepsin he obtained nitrogen corresponding to 3·16% of amide nitrogen, and similar amounts were found with emulsin, rennet, and egg-albumin. Sulphurous acid, which is toxic to living organisms, he found no more poisonous to enzymes than sulphuric acid. The presence of free aldehyde groups in living protoplasm and not in the enzyme is advanced as an explanation. E. Rona[4] is also of the opinion that enzymes do not possess aldehydic properties. In experiments with pepsin, trypsin, amylase, emulsin, invertase, and maltase, he finds that reagents which would condense with an aldehyde group, do not generally render the enzyme inactive provided that the acidity of the medium is suitably adjusted. F. Battelli and L. Stern[5] give further reasons for supposing that oxidising and reducing enzymes are identical.

The influence of pressure on the activity of pepsin, trypsin, and diastase has been studied by S. Fränkel and G. Meldolesi.[6] Pressure usually increases the rate, but the effect diminishes eventually.

R. Willstätter and A. Stoll[7] in 1918 endeavoured to prepare pure specimens of the enzyme peroxydase using the material obtained from horseradish. In another communication[8] a modified method of preparing the extract is described. The peroxydase is found to be almost completely adsorbed by aluminium hydroxide in 50% alcohol, and the greater part of the enzyme is liberated by agitating the adsorption product with an aqueous solution of carbon dioxide. By making use of this property a very active preparation is obtained from horseradish. This line of research is being developed with other enzymes and promises to give important results as to the constitution of enzymes and what is responsible for enzymatic activity.

Amylase.

W. Biedermann[9] contributes two important lengthy papers on diastase. He considers that this enzyme consists of a thermolabile zymogen and a thermostable co-enzyme such as an inorganic salt. The two can be separated by dialysis though difficulty was found in rendering diastase solutions completely inactive by this process.

[3] *Allg. Brau- u. Hopfenzeit.*, 1920, 705; 1921, 121; *J.*, 1921, 273A, 556A.
[4] *Biochem. Zeits.*, 1920, **109**, 279; *J.*, 1921, 22A.
[5] *Chem. Zentr.*, 1921, **92**, I., 332; *J.*, 1921, 273A.
[6] *Biochem. Zeits.*, 1921, **115**, 85; *J.*, 1921, 273A.
[7] *Annalen*, 1918, **416**, 21; *J. Chem. Soc.*, 1918, i., 555.
[8] R. Willstätter and M. Bonner, *Annalen*, 1921, **422**, 47; *J.*, 1921, 125A.
[9] *Fermentforsch.*, 1920-1, **4**, 258, 359; *J.*, 1921, 403A, 523A.

Many salts were found to activate the enzyme, sodium chloride proving specially efficient. This author previously held the opinion that saliva ash is capable of autolysing starch. Others have not been able to repeat his experiments and W. Teschendorf[10] ascribes the autolysis to infection by bacteria. Biedermann now abandons the view, and considers that starch grains contain traces of diastase which are not destroyed in the preparation of the starch. Saliva ash, when added to the starch solution containing traces of enzyme, activates the enzyme and causes the hydrolysis of the starch. By a process of repeated precipitation Biedermann obtains from saliva a substance which he names saliva-albumose. This substance he considers to be the organic zymogen of diastase. It is inactive in aqueous solution, but in the presence of sodium chloride possesses diastatic properties as great as the saliva from which it was prepared.

J. L. Baker and H. F. E. Hulton[11] find that ungerminated rye amylase liquefies potato-starch paste at 50° C. and yields maltose and α-amylo-dextrin (R 1·5; $[\alpha]_D = 184{\cdot}1°$). Barley amylase acts in a similar manner. The amylase of germinated rye under the same conditions gives an unfermentable reducing dextrin (R 10·8; $[\alpha]_D = 181{\cdot}9°$) and maltose. There is no production of intermediate degradable malto-dextrins such as are formed by the action of malt amylase on starch.

Rhizopus tritici is a fungus responsible for large losses of sweet potatoes and other vegetables under storage conditions. L. L. Harter[12] has examined the powdered mycelium of the organism and found it to contain an active diastatic enzyme.

A paper by H. von Euler and O. Svanberg[13] is of interest in connexion with estimation of diastatic power. The initial stage of the action of amylase on a solution of soluble starch is an unimolecular reaction, and the constant of the reaction can be used to measure the activity of the enzyme preparation. The constant K is multiplied by the amount of maltose produced, and the product divided by the amount of enzyme used. This gives a figure (Sf) which characterises the activity of the amylase solution. The authors recommend that the estimation be made at 37° C. and the acidity of the solution be $p_H = 5$. By calculation they find 1000 Lintner units=26Sf. A similar equation has been worked out by these authors to estimate the activity of invertase preparations.[14]

H. Olsson[15] investigated the effect of silver nitrate and aniline on a preparation of amylase. A concentration $2 \times 10^{-7} N$ silver

[10] *Ibid.*, 1920, **4**, 184; *J. Inst. Brew.*, 1921, **27**, 484.

[11] *Chem. Soc. Trans.*, 1921, **119**, 805; *J.*, 1921, 556A.

[12] *J. Agric. Res.*, 1921, **20**, 761; *J. Inst. Brew.*, 1921, **27**, 266.

[13] *Z. physiol. Chem.*, 1921, **112**, 193; *J.*, 1921, 483A.

[14] *Ann. Repts.*, 1920, 423.

[15] *Z. physiol. Chem.*, 1921, **114**, 51; *J.*, 1921, 483A.

nitrate or of 0·15N aniline reduces the activity to one half. W. Windisch,[16] commenting on the great effect of salts of heavy metals on the activity of amylase, points out that this effect is not likely to occur in the mash tub, for proteins and salts are present in abundance. These would precipitate the metal and render it inactive.

M. Samec and A. Mayer[17] show that formaldehyde does not effect a degradation of starch at the ordinary temperature but converts it into a loose compound which is not coloured by iodine.

Invertase.

Most yeasts of technical importance contain invertase, and the enzyme is present in other micro-organisms.

H. von Euler[18] gives the relative activity of the enzyme in four organisms as follows:—Bottom fermentation yeast 100, top fermentation yeast 60, *Penicillium glaucum* 10, *Aspergillus niger* 2.

Invertase preparations can be made from yeast, and several communications by H. von Euler and O. Svanberg[19] on the properties of such preparations have appeared of late.

Silver and mercury salts have a strong inhibiting effect on the enzyme, but the activity of the enzyme can be restored by precipitating the metal with hydrogen sulphide The possibility of an –SH group in invertase is suggested. Aniline also renders the enzyme inactive, but the activity can be wholly restored by dialysis. In the case of poisoning by silver and mercury the activity can only be partly restored by this process. Analyses of highly active preparations of invertase obtained by dialysis show the presence of phosphorus, and the activity of the preparation was found to be approximately proportional to the amount of phosphorus present.[20] A dried invertase preparation gave 0·16% P, 1·27% N, 91·5% hexoses.

R. Willstätter and F. Racke[21] contribute an important paper on invertase obtained from yeast. These authors use a new method of preparation similar to that employed in isolating peroxydase. They make use of the fact that the enzyme is adsorbed by aluminium hydroxide and by kaolin. They succeeded in obtaining highly-purified specimens, more active than any so far obtained and free from albuminoids and yeast gum.

[16] *Woch. Brau.*, 1921, **13**, 165.

[17] *Koll.-Chem. Beih.*, 1920, **13**, 165; *J. Chem. Soc.*, 1921, **120**, i., 400.

[18] *Fermentforsch.*, 1921, **3**, 242.

[19] *Ibid.*, 1920, **4**, 29, 90, 142; *J.*, 1921, 483A.

[20] *Z. physiol. Chem.*, 1921, **112**, 282; *J.*, 1921, 482A.

[21] *Annalen*, 1921, **425**, 1.; *J. Chem. Soc.*, 1921, **120**, i., 823.

Maltase.

Maltase is an enzyme which is specially sensitive to acids. R. Willstätter, T. Oppenheimer, and W. Steibelt [22] find that the enzyme can be extracted from fresh yeast in the presence of toluene if precautions are taken to keep the solution neutral. The continual addition of small amounts of 1% ammonia is one method of ensuring this neutrality. Another method which gives satisfactory results is to carry out the extraction in the presence of magnesium carbonate. The velocity of hydrolysis of maltase in solutions $p_H = 6{\cdot}6$ was found to be proportional to the concentration of the enzyme present. R. Willstätter and W. Steibelt[23] find that the well-known toxic action of chloroform on maltase can be prevented by the addition of a suitable phosphate mixture to maintain the favourable alkalinity. This con rms the conclusions of W. A. Davis,[24] who attributed the toxic action of chloroform on maltase prepared from plants to the presence of traces of acid or alkali.

Carboligase.

This is the name given to the enzyme of yeast which is shown by C. Neuberg and J. Hirsch [25] to cause condensations of the benzoin type. If benzaldehyde is added to a solution of sugar which is undergoing alcoholic fermentation by yeast, a hydroxyketone $C_6H_5{\cdot}CO{\cdot}CHOH{\cdot}CH_3$ is formed. This is attributed to the interaction of benzaldehyde and pyruvic acid, the latter being an intermediate compound in alcoholic fermentation. Yeast acts on the two aldehydes producing the same substance, but in the absence of yeast no reaction takes place.

Fermentation.

The chemical mechanism of alcoholic fermentation is still attracting attention, and further evidence of the intermediate formation of pyruvic acid and acetaldehyde is forthcoming. C. Neuberg and E. Reinfurth [26] use a new reagent to "fix" the acetaldehyde formed as an intermediate compound during fermentation. Dimethylhydroresorcinol readily forms condensation products with aldehydes, and if fermentation is carried out in the presence of this substance, the insoluble condensation product settles out with the yeast. The amount of aldehyde "fixed" by this method is less than that "fixed" by a sulphite.

[22] *Z. physiol. Chem.*, 1920, **110**, 232; *J. Inst. Brew.*, 1921, **27**, 193.
[23] *Ibid.*, 1920, **111**, 157; *J.*, 1921, 55A.
[24] *Biochem. J.*, 1916, **10**, 34.
[25] *Biochem. Zeits.*, 1921, **115**, 282; *J.*, 1921, 404A.
[26] *Ibid.*, 1920, **106**, 281; *J. Inst. Brew.*, 1921, **27**, 41.

Zinc and cadmium salts, according to S. Kostytschew[27] and his co-workers, S. Subkowa and L. Frey, act on the reducing enzymes of yeast rendering them inactive. If alcoholic fermentation is carried out by dead yeast cells in the presence of these salts, large amounts of aldehyde are produced. The absence of reducing enzymes, which transform aldehyde to alcohol, accounts for this result.

Aldehyde appears to play an important part in the decomposition of sugar in many biochemical processes. C. Cohen[28] finds it during the fermentation of dextrose by moulds, and C. Neuberg, F. F. Nord, and E. Wolff[29] can detect it when *B. lactis aerogenes* acts on this sugar.

C. Neuberg and W. Ursum[30] have further investigated the effect of alkaline substances on fermentation. Under such conditions some of the aldehyde is transformed into ethyl alcohol and acetic acid, and the final products consist of glycerol, acetic acid, ethyl alcohol, and carbon dioxide.

The initial stages of alcoholic fermentation by preparations from yeast proceed comparatively slowly. This period of induction has been investigated by A. Harden and F. K. Henley,[31] who find that the reaction is much accelerated by the addition of aldehyde and methylene blue. They attribute the slowness of the initial stages of fermentation to the absence of a hydrogen acceptor which is normally formed in a later stage of fermentation.

$$CH_3{\cdot}CO{\cdot}COOH \rightarrow CH_3CHO + CO_2 \rightarrow CH_3{\cdot}CH_2{\cdot}OH + CO_2.$$

The influence of salts on this induction period has also been investigated. In living yeast the absence of catalysts of an aldehydic nature [illegible] occurs, and these induction periods are either absent or much less pronounced.

C. Neuberg and M. Sandberg[32] have tested the influence of 71 aldehydes on fermentation and found an accelerative influence in all cases. The effect on fermentation by yeast maceration juice is most marked.

Fermentation by living yeast differs in many ways from that by yeast juice, dried yeast, and other preparations of yeast. The writer pointed out some years ago[33] a difficulty in applying Harden's equations of alcoholic fermentation to living yeast J. Giaja[34] does good service in pointing out some other differences.

[27] *Z. physiol. Chem.*, 1920, **111**, 126, 132 ; *J.*, 1921, 56A.
[28] *Biochem. Zeits.*, 1920, **112**, 139 ; *J.*, 1921, 56A.
[29] *Ibid.*, 1920, **112**, 144 ; *J.*, 1921, 56A.
[30] *Ibid.*, 1920, **110**, 193 ; *J. Inst. Brew.*, 1921, **27**, 133.
[31] *Biochem. J.*, 1920, **14**, 642 ; 1921, **15**, 175, 313 ; *J.*, 1921, 524A.
[32] *Biochem. Zeits.*, 1920, **109**, 290 ; *J.*, 1921, 93A.
[33] *J. Inst. Brew.*, 1911, **17**, 153.
[34] *Brass. et Dist.*, 1921, **19**, 323 ; *J. Inst. Brew.*, 1921, **27**, 479.

Zymase has a fermentative activity only about 5% of that of the original yeast from which it is prepared. The addition of toluene to living yeast also reduces the activity to about the same extent. This great diminution does not admit of easy explanation, and Giaja considers that only about 5% of the activity of living yeast is due to zymase, and that the main part of fermentation proceeds by some other process. The possibility that living yeast contains stimulants to zymase and that these are absent in yeast juice may, however, account for the great activity of living yeast.

The fermentation of galactose shows peculiarities which do not occur in the fermentation of dextrose, lævulose, and mannose. Some yeasts, if grown in a nutrient medium containing galactose, ferment this sugar, other yeasts do not. Moreover, if yeasts which give positive results when tested in this manner are introduced into a solution of pure galactose, very little evolution of carbon dioxide takes place, unless growth in the presence of the sugar occurs. The present writer found that the rate of fermentation of galactose by yeast grown in wort was less than 1% of that of glucose.[35] H. von Euler, I. Laurin, and A. Petterson[36] find the rates of fermentation of the two sugars by a top fermentation yeast to be in the ratio 1 to 50. If correction were made for the autofermentation of the yeast the rates would diverge still further. It is doubtful if any galactose at all disappears under these circumstances. Yeast grown in the presence of galactose gives a crop which ferments the sugar, in some cases even more rapidly than glucose. The means by which yeast adapts itself to ferment this sugar is of much interest, and has been studied by H. von Euler and his collaborators. Aqueous extracts of dried yeast accelerate the process, and he obtains an adaptation of the yeast by previous treatment of the yeast with galactose solution. The adaptation can take place apparently without a cell increase, though when large amounts of yeast are put into a galactose solution some of the cells die, and yeast counts may not detect the production of new yeast. H. E. Armstrong[37] expresses doubt as to the capability of yeast to adapt itself to ferment galactose, and regards the production of an active yeast as due to the survival and growth of a few cells which possess this property.

If, however, one starts with a single yeast cell which does not ferment galactose, and by suitable growth obtains a yeast crop which does ferment the sugar, adaptation or acclimatisation has taken place somewhere. The fermentation of galactose is of little technical interest, but it affords an example of the influence of

[35] *Chem. Soc. Trans.*, 1908, **93**, 224; *J.*, 1908, 241.
[36] *Biochem. Zeits.*, 1921, **114**, 277.
[37] *J. Inst. Brew.*, 1921, **27**, 230.

environment on the characteristics of micro-organisms, and this is of much importance.

J. O'Sullivan[38] publishes some experiments on the fermentation of worts containing added sugars. He finds that when cane sugar, invert sugar, maltose, or dextrose is added to the extent of 15% to malt wort of an original gravity of 1061 degrees, all the fermentable sugars are acted on by the yeast. If larger quantities of sugar are added some of the sugar is left unfermented. The retarding influence of the alcohol produced is great as soon as the concentration amounts to 5% by volume.

ANALYSIS.

Malt.

The extract from coloured malts, flaked maize, and similar brewing materials, is estimated by mashing, either with malt or with an aqueous extract of malt. In the method recommended by the committee of the Institute of Brewing, malt extract is used, and this method has the advantage in that only a small correction is required for the extract which is added to bring the material into solution. C. G. Matthews[39] gives reasons for preferring the use of malt itself. He mashes 40 g. of standard malt (diastatic capacity 35°–45° Lintner) with 10 g. of coloured malt. In spite of the large correction, due to the addition of so much standard malt, he concludes that this method gives usually more reliable results.

W. Windisch and P. Kolbach[40] have studied various methods of obtaining the extract of raw grain (maize and rice). They recommend filtered malt extract for the purpose of dissolving the material, and give details as to time and temperature. C. Chabot and M. H. van Laer[41] describe some experiments on determinations of malt extracts. They find that by adjusting the acidity of the mash, they obtain higher extracts which more closely approach those found in practice. F. Eckhardt[42] finds the analysis of brewery grains of value in controlling brewery extracts. He estimates the percentage of moisture, the specific gravity of the liquid obtained by pressing the grains in a small hand press, and the percentage of undissolved extract remaining in the grains. This undissolved extract is obtained in solution by use of malt extract.

In determining extracts, original gravities, and densities of various solutions, a pyknometer is generally used. Variations in barometric pressure make slight differences in the apparent weight

[38] *Ibid.*, 1921, **27**, 93; *J.*, 1921, 273A.
[39] *Ibid.*, 1921, **27**, 22; *J.*, 1921, 158A.
[40] *Woch. Brau.*, 1921, **38**, 57; *J.*, 1921, 444A.
[41] *Bull. Soc. Chim. Belg.*, 1921, **30**, 253; *J.*, 1921, 745A.
[42] *Z. ges. Brauw.*, 1921, 81; *J.*, 1921, 597A.

of the vessel, and if great accuracy is desired, corrections have to be made. H. Keil[43] describes a method of making these corrections automatic. He uses a counterpoise of approximately the same weight and volume as the pyknometer when the latter is filled with water. The method has received official recognition in Germany.

Several communications on the diastatic power of malts have appeared during the year, though there is nothing very novel to record. J. L. Baker and H. F. E. Hulton[44] prefer the iodometric method of estimating the maltose formed by the action of malt extract on soluble starch. The method employed by W. Windisch[45] and P. Kolbach is very similar. G. Roeder[46] suggests a method which closely approximates to that recommended by the Institute of Brewing Committee.[47] There seems little reason to depart from this latter method, except in the one particular discussed in last year's report.[48] A "buffer" salt to ensure neutrality during the action of malt extract on the soluble starch is a distinct advantage.

Alcohol.

A. Lachman[49] describes a rapid volumetric method of determining alcohol in aqueous solutions containing 20% of alcohol and more. The method depends on the solubility of aniline in mixtures of alcohol and water. A definite weight of aniline (25 g.) is mixed with a definite volume (50 c.c.) of aqueous alcohol, the strength of which is to be found. Water is added until turbidity occurs. From the volume of water required the strength of the alcohol can be determined. Several corrections have to be made, and tables are necessary to carry out the calculations. In control work with samples varying to a comparatively limited extent, the author claims that the method is rapid and accurate. H. Rosset[50] describes a somewhat similar method for estimating the strength of fairly concentrated solutions of alcohol. The method depends on a determination of the miscibility temperature of a mixture of acetone, petroleum spirit, and aqueous alcohol. The presence of methyl alcohol in ethyl alcohol is usually detected by oxidising the mixture and testing for formaldehyde. F. Rabe[51] recommends the use of resorcinol-sulphuric acid for the purpose. Modifications

[43] *Woch. Brau.*, 1921, **38**, 95; *J.*, 1921, 444A.
[44] *Analyst*, 1921, **46**, 90; *J.*, 1921, 272A.
[45] *Woch. Brau.*, 1921, **38**, 149; *J.*, 1921, 597A.
[46] *Ibid.*, 1921, **38**, 5; *J.*, 1921, 158A.
[47] *J. Inst. Brew.*, 1906, **23**, 6.
[48] *Ann. Repts.*, 1920, **5**, 430.
[49] *J. Ind. Eng. Chem.*, 1921, **13**, 230; *J.*, 1921, 274A
[50] *Ann. Chim. Analyt.*, 1921, **3**, 235; *J.*, 1921, 712A.
[51] *Pharm. Zeit.*, 1921, **66**, 72; *J.*, 1921, 159A.

of the well-known method of Denigès, in which formaldehyde is estimated colorimetrically by Schiff's reagent, are suggested by R. M. Chapin[52] and by R. Sieber.[53]

Starch.

Recent advances in the chemistry of starch are discussed elsewhere, and reference is made here only to two papers which are of interest in the estimation of starch in the raw material of the fermentation industries.

The taka-diastase method elaborated by Davis and Daish[54] has been used by E. Horton[55] to estimate starch in wheat. He found that the apparent amount of starch varied according to the amount of enzyme used, and different specimens of enzyme gave different results. He therefore reinvestigated the method, and came to the disappointing conclusion that it cannot be implicitly trusted. Even in skilful hands inconsistent results are obtained. The evidence on the whole points to incomplete conversion of dextrin into dextrose and maltose by the enzyme preparation. C. Mannich and K. Lenz[56] describe a method of estimating starch by dissolving it in boiling calcium chloride solution, which is made slightly acid ($N/500$) with acetic acid. The solution is filtered and the starch estimated by the polarimeter. If other optically active substances are present, correction has to be made for them. This is done by carrying out a "blank" experiment using cold calcium chloride solution, which dissolves these substances but does not dissolve starch.

General.

The importance of the hydrogen-ion concentration in worts and beers is generally recognised, and descriptions of measurements of such concentrations, and some applications of the results, are given by R. H. Hopkins[57] and by L. S. Medalia.[58] The refractometer is an instrument which would probably find more application in the fermentation industries if it were not so expensive. K. Geys[59] uses the Zeiss instrument for determining the strength of worts in malt analysis, and finds that such determinations agree well with those estimated by the pyknometer. This refractometer is also used by W. Lange and G. Reif[60] to estimate methyl and ethyl alcohols in spirits, medicines, etc.

[52] *J. Ind. Eng. Chem.*, 1921, **13**, 543; *J.*, 1921, 712A.
[53] *Papier-Fabr.*, 1921, **19**, 189; *J.*, 1921, 274A.
[54] *J. Agric. Sci.*, 1914, **6**, 152; *J. Inst. Brew.*, 1914, **20**, 718.
[55] *Ibid.*, 1911, **11**, 240; *J. Inst. Brew.*, 1920, **27**, 594; *J.*, 1921, 745A.
[56] *Z. Unters. Nahr. Genussm.*, 1920, **40**, 1; *J. Inst. Brew.*, 1921, **27**, 327.
[57] *J. Inst. Brew.*, 1921, **27**, 401.
[58] *Bull. Bureau Biotechn.*, 1921, **3**, 55; *J. Inst. Brew.*, 1921, **27**, 561.
[59] *Z. ges. Brauw.*, 1921, 106; *J.*, 1921, 597A.
[60] *Z. Unters. Nahr. Genussm.*, 1921, **41**, 216; *J.*, 1921, 598A.

A. R. Ling and D. R. Nanji[61] describe an improved method of estimating pentoses and pentosans. The material is distilled with 12% hydrochloric acid and the furfural collected in the distillate. The furfural is subsequently precipitated with phenylhydrazine and the excess of the latter reagent estimated by means of iodine solution. A sample of arabinose estimated by this method and by the phloroglucinol method gave results in close agreement.

The usual method of estimating sulphurous acid in wines, beers, etc. consists in distilling the liquid with phosphoric acid in an atmosphere of carbon dioxide. The sulphur dioxide is collected in a solution of iodine, and the sulphuric acid produced estimated gravimetrically. V. Froboese[62] recommends distillation into sodium bicarbonate solution, oxidation of the sulphite with hydrogen peroxide, and titration of the excess of alkali with standard hydrochloric acid.

Macheleidt[63] describes a gravimetric method of estimating carbon dioxide in beer. The bottle of beer is cooled to prevent escape of gas, and then opened. Ammonia is immediately added and then 'magnesia mixture' to precipitate phosphates. The carbonate in the filtrate from such solutions is estimated by precipitation with calcium chloride, and subsequently converting the calcium carbonate into oxide by ignition. The writer described last year a method of estimating carbon dioxide by distillation under reduced pressure.[64] The apparatus can be easily adapted to estimate carbon dioxide in beer.

Barley and Malt.

A detailed account of the harvesting, storage, and drying of barley is given by A. Cluss, W. Kluger, and V. Koudelka.[65] The experiments were carried out on 1913 barleys and 1914[66] barleys. To improve the quality and germinating power of the grain they recommended drying to reduce the moisture contents to about 12%. The best time they consider to carry out the process is after about 6 weeks' storage.

The influence of the quantity of seed, and the method of sowing, on the yield of barley has been examined by R. Iversen[67] in Denmark. Seed sown broadcast gives results almost as satisfactory as when the seed is sown in lines 10 cm. apart. The quantity of seed is of more importance than the method of sowing.

[61] *Biochem. J.*, 1921, **15**, 466; *J. Inst. Brew.*, 1921, **27**, 562; *J.*, 1921, 752A.

[62] *Chem. Zentr.*, 1921, **92**, IV., 225; *J.*, 1921, 641A.

[63] *Z. ges. Brauw.*, 1921, 130; *J.*, 1921, 634A.

[64] *J.*, 1921, 149T.

[65] *Z. ges. Brauw.*, 1920, **43**, 353, 361; *J.*, 1921, 22A.

[66] *Ibid.*, 1921, **44**, 4.

[67] *J. Inst. Brew.*, 1921, **27**, 474.

G. von Ubisch[68] has studied from a botanical point of view the crossing of *H. Spontaneum* with different varieties of cultivated barley. Other results obtained by cross-breeding barleys on Mendelian lines are described by F. L. Engledow.[69]

Some useful information about the 1920 crop of barley of British and foreign sources is given by J. Stewart[70] in a review on the barley situation.

Bavarian barleys of 1921 are discussed by G. Fries.[71] The moisture contents he finds low, averaging 13·4%. Nitrogen occurs in normal amount. Starch contents and extracts are high, and the germination is good.

G. Gentner[72] describes an aërobic rod-shaped micro-organism (*B. cerealium*) which causes brown stains on the stem and leaves of the barley plant. T e bacillus can attack damp barley, and is not easily eradicated by treatment of the grain with antiseptics.

F. A. Mason[73] contributes a very useful summary of the injurious insects which can destroy barley and malt. An account of the effect of asphyxiating agents on some of these insects is given. *Trogoderma khapra*, a beetle probably brought over in shipments of Indian barley, is a new pest to this country. It is specially resistant to adverse circumstances, but the application of hypochlorites and fumigation with chlorine proved to be efficient in destroying the insect.

Hops.

The investigation of hops is one of the prominent features in the Institute of Brewing Research Scheme. The breeding of new varieties is taking place at the South Eastern Agricultural College, Wye, and at the East Malling Research Station. An account of the distinctive characteristics of 22 new varieties grown in 1920 is given by E. S. Salmon.[74] They have been examined with regard to fruitfulness, aroma, resins, and resistance to disease. Many of these hops have now been grown for four years, and some interesting facts are coming to light. Several characteristics of the hops have appeared each year. The high or low total-resins-content remains relatively constant for each variety. The percentage of hard resin to total resin is a distinctive varietal character.

[68] *Ibid.*, 1921, **27**, 80.
[69] *J. Agric. Sci.*, 1921, **11**, 159; *J. Inst. Brew.*, 1921, **27**, 551.
[70] *J. Inst. Brew.*, 1921, **27**, 296.
[71] *Z. ges. Brauw.*, 1921, 161; *J. Inst. Brew.*, 1921, **27**, 588.
[72] *Ann. Brass. et Dist.*, 1921, **19**, 201; *J. Inst. Brew.*, 1921, **27**, 187.
[73] *J. Inst. Brew.*, 1921, **27**, 348.
[74] *Ibid.*, 1921, **27**, 451.

A. H. Burgess[75] contributes a communication on the drying of hops. Temperature records made with self-registering thermometers were taken in fifteen oastings of hops. The temperatures of drying vary in kilns between 135° F. and 183° F., the average being 158° F.

A description of hop-picking by machinery is given in the *Brewers' Journal.*[76]

E. S. Salmon[77] publishes some useful information on the control of hop "mould." Great stress is laid on the efficacy of early sulphuring. Unadulterated flowers of sulphur is recommended for the purpose, and the disinfecting should be started in May.

A. R. Ling and D. R. Nanji[78] describe a rapid polarimetric method of estimating tannin in hops. The method is a modification of the one elaborated by A. C. Chapman.[79] The process consists in precipitating the tannin in the hop extract with cinchonine sulphate. Whilst in Chapman's method the cinchonine tannate is collected and weighed, in the new method the amount of cinchonine precipitated by a definite extract of hops is estimated by the polarimeter. In spite of the change in rotation of the solution being rather small, the results show satisfactory accuracy.

Brewing.

The chemical reactions which occur in the mash tub can only be satisfactorily carried out in slightly acid solution. The presence of "buffer" salts and the natural acidity of malt usually ensures this acidity. The removal or neutralisation of bicarbonate in brewery water before mashing may in certain cases be advisable, and is a matter which has been frequently discussed. Softening the water with lime and the lactic acid treatment are critically examined by F. M. Maynard.[80] P. Petit[81] suggests the addition of sulphuric acid. The method is no doubt effective, but hardly to be recommended.

The use of malt substitutes for brewing purposes is now permitted in Germany. W. Windisch[82] gives a description of the brewing properties of maize and rice. He finds no deterioration in the yeast when these adjuncts are used in reasonable amounts.[83] Many German malts he finds lacking in diastase and unsuitable

[75] *Ibid.*, 1921, **27**, 180; *J.*, 1921, 362A.

[76] *Brewers' J.*, 1921, 426.

[77] *J. Ministry Agric.*, 1921, **28**, 150; *J. Inst. Brew.*, 1921, **27**, 392.

[78] *J. Inst. Brew.*, 1921, **27**, 310; *J.*, 1921, 556A.

[79] *Ibid.*, 1907, **13**, 646.

[80] *Ibid.*, 1921, **27**, 493; *Brewing Trade Review*, 1921, 417.

[81] *Brass. et Malt.*, 1921, **10**, 321; *J. Inst. Brew.*, 1921, **27**, 130.

[82] *Woch. Brau.*, 1921, **38**, 9; *J.*, 1921, 158A.

[83] *Ibid.*, 1921, **38**, 52; *J. Inst. Brew.*, 1921, **27**, 269.

for the purpose of mashing with raw grain.[84] L. Mélard[85] contributes an interesting account of the action of proteins in the brewing process, and many of his conclusions agree with H. T. Brown's well-known work on the subject. He considers that worts should not contain too much assimiable nitrogen, as they ferment slowly and give rise to an unstable beer. H. T. Brown, on the other hand, whilst obtaining many valuable results in his work on the subject, finally came to the conclusion that there is no very definite relationship between assimiable nitrogen and the subsequent growth of bacteria and wild yeast in the beer.[86]

P. Petit[87] finds that worts brewed from 1921 malts (in France) do not ferment sufficiently far in the brewery. He recommends the addition of a vigorously fermenting sugar solution in place of the usual wort Kräusen to ensure a more complete fermentation.

F. Schönfeld[88] summarises his views on the factors which influence the "secondary" fermentation of (lager) beer. The fermentation he discusses is in reality a continuation of the primary fermentation in the lager vessels. He points out that the presence of a fermentable sugar, and sufficient yeast in suspension, are two big factors controlling this conditioning of the beer. The tendency of the yeast to clot and fall to the bottom of the vessel, the fermentative activity of the yeast, agitation, and temperature of storage, also play a part. Of great importance is the small quantity of oxygen absorbed by the beer on transference to the lager vessels. This absorption causes a re-growth of the primary yeast and an increased after-fermentation. He further points out that the yeast at this time tends to get covered with an albuminoid deposit from the beer, and this causes the yeast to coagulate and lessens its activity. Yeast has a means of protecting itself against this albuminoid "poison," as it contains peptic enzymes which exert a solvent action on the mucous layer. These results are of interest to brewers in this country, for the fermentation discussed by Schönfeld corresponds to the conditioning of beers in cask after racking. The use of "priming" to supply an easily fermentable sugar, the importance of having a certain amount of primary yeast left in the beer, the influence of oxygen, and the effect of colloidal substances precipitated from the wort, are all matters which have been discussed by our chemists.

E. R. Moritz[89] contributes an interesting paper on refrigeration and flocculation. Worts containing unflocculated amorphous

[84] *Ibid.*, 1921, **38**, 143; *J. Inst. Brew.*, 1921, **27**, 477.
[85] *Brass. et Dist.*, 1921, **19**, 348, 364; *J. Inst. Brew.*, 1921, **27**, 475.
[86] *J. Inst. Brew.*, 1916, **22**, 343.
[87] *Brasserie and Malterei*, 1921, **11**, 129; *J. Inst. Brew.*, 1921, **27**, 519.
[88] Through *Brewing Trade Review*, 1921, 290.
[89] *J. Inst. Brew.*, 1921, **27**, 525.

matter produce beers which tend to show a haze and are liable to wild yeast troubles. To overcome these troubles, H. T. Brown advocated agitation of the wort during cooling to aid flocculation. Moritz gives as his experience, that a long smooth travel of the wort in the refrigerator is the best means of obtaining the desired flocculation, though, so far, no explanation of the result is forthcoming.

Oxalates occur in small quantities in brewery worts. Calcium oxalate mixed with organic substances is deposited as a hard layer on the surface of the refrigerator tubes, wort mains, and fermenting vessels. This scale is objectionable and difficult to remove. The origin of the oxalic acid is of some interest. A Bau,[90] by use of the calcium acetate reagent, finds 0·004% of oxalic acid in fresh hopped beer wort. Unhopped wort contained about half the amount. Hops showed from 0·57 to 0·65%, calculated on the dried substance. Sterile hopped wort, after standing seven months showed rather more than 80% of the total oxalate in the residue, leaving only 0·0007% in solution.

Brewery plant is at the present time receiving a considerable amount of critical examination. The mash tub is considered an inefficient vessel, and its replacement by a mash filter is advocated by F. M. Maynard.[91] The claim is made that it is possible to work with finely ground malt, and that higher extracts and more concentrated wort are obtained. Many other suggestions regarding the practical application of modern methods in the brewery are given in the publication.

L. Pierre[92] discusses some recent improvements in steam-heated coppers. He estimates that the amount of steam required to evaporate 1 lb. of water from the wort is, in practice, about 1·67 lb. If it were possible to recover the heat from the steam of the boiling wort, and use it efficiently, the consumption of only 0·67 lb. of steam from the boiler would be necessary. To obtain this economy he proposes to use a jet of live steam from an injector to compress the steam from the boiling wort, and send it, mixed with the injector steam, into the heating coil of the copper.

In the Burton union system of cleansing beers, the latter part of the fermentation takes place in a series of casks each of capacity about 150 gallons. An improvement in the process is taking place at the present time. It has been found possible to replace the oak casks by a large metal cylindrical drum, fitted with "swan necks," which discharges the barm into a trough in the usual manner.

G. Defourny[93] describes a method of increasing the efficiency

[90] *Woch. Brau.*, 1921, **38**, 113; *J.*, 1921, 557A.
[91] *J. Inst. Brew.*, 1921, **27**, 499; *Brewing Trade Review*, 476.
[92] *Ann. Brass. et Dist.*, 1920, **10**, 277; *J. Inst. Brew.*, 1921, **27**, 86.
[93] *Ann. Brass. et Dist.*, 1921, **19**, 216; *J. Inst. Brew.*, 1921, **27**, 263.

of the refrigerator in breweries. The device consists in restricting the inner area of the tubes by the presence of interior smaller tubes closed at both ends. The cooling water circulates in the narrow annular spaces, so produced, and is thus used more efficiently.

H. Lloyd Hind[94] gives an interesting account of the bottling plant of the Carlsberg brewery. Nineteen-twentieths of the output of the brewery is bottled, and the arrangements are such as to deal with over a million bottles per day.

A concise account of the processes involved in malting and brewing is given by A. L. Stern in Vol. I. of *Thorpe's Dictionary of Applied Chemistry.*

F. M. Maynard has continued during the year his detailed description of lager beer brewing.[95]

DISINFECTANTS.

Disinfectants find much use in the fermentation industries, for in the preparation and storage of the raw material, and in all stages of the fermentation process, damage is likely to occur owing to the action of insect pests and micro-organisms. The record of the experience of various investigators is therefore of interest. In the work by F. A. Mason on malt and barley pests, to which reference has already been made, chlorine and hypochlorites were found of great use in eradicating the insects. Other disinfectants are discussed. Carbon bisulphide was at one time recommended by the Board of Agriculture, but now finds less favour. Like benzene, which is also efficacious against all insects, it is highly inflammable, and the use involves considerable risk. Experiments with pentachloroethane are described by T. Parker and A. W. Long.[96]

E. K. Rideal and U. R. Evans,[97] in discussing the use of hypochlorites, show that the germicidal action is closely allied to the oxidising power, and this is greatly depressed in alkaline solutions. Acid solutions are therefore likely to be more effective than alkaline ones for disinfecting purposes, though for storing such solutions alkaline ones are to be preferred, as they are more stable. R. Heuss[98] investigated the germicidal power of hypochlorites prepared on a small scale electrolytically. He found that as far as wild yeasts are concerned hypochlorite solutions, though alkaline, are effective disinfectants.

P. Malvezin[99] proposes the use of formaldehyde-sulphurous acid $CH_2(OH)SO_3H$ for disinfecting. A 1% solution sprayed

[94] *J. Inst. Brew.*, 1921, **27**, 25.

[95] *Brewers' J.*, 1921, 40, etc.

[96] *Bull. Bureau of Biotechnology*, 1921, 104.

[97] *J.*, 1921, 64R.

[98] *Z. ges. Brauw.*, 1919, **42**, 351; *J. Inst. Brew.*, 1920, **26**, 265.

[99] *Bull. Assoc. Chim. Sucr.*, 1921, **38**, 210; *J. Inst. Brew.*, 1921, **27**, 265.

matter produce beers which tend to show a haze and are liable to wild yeast troubles. To overcome these troubles, H. T. Brown advocated agitation of the wort during cooling to aid flocculation. Moritz gives as his experience, that a long smooth travel of the wort in the refrigerator is the best means of obtaining the desired flocculation, though, so far, no explanation of the result is forthcoming.

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[91] *J. Inst. Brew.*, 1921, **27**, 499; *Brewing Trade Review*, 476.

[92] *Ann. Brass. et Dist.*, 1920, **10**, 277; *J. Inst. Brew.*, 1921, **27**, 86.

[93] *Ann. Brass. et Dist.*, 1921, **19**, 216; *J. Inst. Brew.*, 1921, **27**, 263.

the nitroprusside reaction which serves as a guide in the difficult process of isolating the substance. Observations are described which show that the dipeptide exercises real functions in the chemical dynamics of the cell. The substance is autoxidisable, and owing to changes in the sulphur group [—SH+HS— $\leftrightarrows$ —S.S— + H_2] it acts under varying conditions, either as a hydrogen acceptor or an oxygen acceptor.

The acidity of the medium is an important factor in these oxidations and reductions. The dipeptide seems to possess catalytic properties which enable it to play a part in cell oxidations.

Apart from the general importance of the publication, the information regarding the production of traces of hydrogen sulphide by yeast is of some technical interest.

An attempt has been made by A. Slator[105] to work out the theory of yeast crops and to express the amount of yeast a given nutrient medium will produce in terms of generation-times and fermentative activity of the yeast. If conditions are so arranged that the sugar is the limiting factor which finally stops the growth, the yeast crop is determined by the way the ratio K/F varies with different concentrations of sugar where K is the constant of growth and F the fermentative activity of the yeast.

Yeast crops obtained from a medium containing small amounts of sugar were found to agree with those calculated from measurements of K and F.

By carrying out experiments in sealed tubes and allowing the carbon dioxide to accumulate, it was found possible to make the carbon dioxide the limiting factor determining the crop. With varying amounts of actively growing seeding a constant cell increase was observed. The influence of temperature on the crop is comparatively small. The following table gives the generation-time in hours of a brewery yeast, the constant of growth K, the fermentative activity F, *i.e.*, the number of grams of sugar fermented per hour per yeast cell.

Temp.	G.T.	K.	F.	K/F.
10° C.	11·6	0·060	$12·5 \times 10^{-12}$	4800×10^6
15°	6·4	0·108	24·5	4400
20°	2·95	0·235	47·0	5000
25°	1·77	0·392	75·0	5200
			Average	4900×10^6

[105] *Chem. Soc. Trans.* 1921, **119**, 115; *J.*, 1921, 234A.

The influence of temperature on growth and fermentation is very great, but the ratio remains fairly constant. The average figure, 4900×10^6, represents the number of yeast cells produced when one gram of sugar disappears. If this ratio could be maintained throughout the whole of the fermentation, the very large crop of about 1 g. of pressed yeast to 1 g. of sugar fermented would be obtained. Attempts to make oxygen the limiting factor controlling the crop were not successful.

In this work concentrations of yeast were determined by centrifuging the suspension in a graduated capillary tube. A method of the kind was used by T. Carlson[106] and by K. Schweizer.[107] E. Kohler[108] discusses the relationship between fermentation and growth. He considers it probable that the fermentative enzymes are present in the outermost layers of the cell plasma, and separated from the medium only by the cell membrane.

H. Lucrs and R. Heuss[109] have made a study of the flocculation of yeast. The rate at which yeast cells settle out in a fermenting liquid is of importance, for this factor plays a part in determining the amount of fermentable sugars left in the beer, the brightness of the beer, and the amount of yeast obtained. In aqueous suspensions of living yeast they trace a relationship between flocculation and viscosity of the suspension. Marked flocculation of the yeast corresponds to a high viscosity. The reaction of the medium is of importance. With a solution showing $p_H = 4{\cdot}0$—$3{\cdot}1$ flocculation is good and viscosity is high, with $p_H = 4{\cdot}9$ the viscosity is low and no flocculation takes place. In worts the matter is much more complicated owing to the presence of colloids.

R. J. B. Storey[110] contributes a note on the difficulties in keeping brewery yeast in good condition. He advocates two well-established processes, the treatment of yeast with tartaric acid to free it from bacteria, and the storing of pitching yeast at a low temperature. French breweries favour phosphoric acid in place of tartaric acid to eliminate bacterial infection.[111]

Yeast is sometimes washed with dilute sulphuric acid to kill any bacteria present. W. Henneberg and M. Böhmer[112] show that the condition of the yeast cell is a factor of importance in this treatment. Quiescent yeast cells are much more resistant to acid than actively-growing cells are. Other interesting observations regarding the toxic action of sulphuric acid on yeast are included in this publication.

[106] *Biochem. Zeits.*, 1913, **57**, 513; *J. Inst. Brew.*, 1914, **20**, 436.
[107] *Bull. Assoc. Chim. Sucr.*, 1920, **38**, 163; *J.*, 1921, 191A.
[108] *Woch. Brau.*, 1921, **38**, 65; *J. Inst. Brew.*, 1921, **27**, 443.
[109] *Z. ges. Brauw.*, 1921, 18; *J.*, 1921 362A.
[110] *J. Inst. Brew.*, 1921, **27**, 102.
[111] *Ann. Brass. et Dist.*, 1921, **20**, 30; *J. Inst. Brew.*, 1921, **27**, 591.
[112] *Woch. Brau.*, 1921, **38**, 237; *J.*, 1921, 864A.

C. G. Frazer[113] has tested the effect of ten stains on yeast, and finds methylene blue and erythrosin the most satisfactory to distinguish living from dead cells. Dead cells are stained within one minute, and living cells are not stained at all.

Vitamins.

Much work on vitamins is being carried out at the present time, and some of it is of considerable importance to the fermentation industry. Yeast contains vitamin B, the antineuritic food accessory substance. Research is proceeding at the present time to determine (1) if yeast synthesises this vitamin, or if it collects it from the medium in which it grows, (2) if the growth of yeast cells can be used as a test for any of the vitamins, and if this test can be made in any way quantitative. A preliminary note by A. Harden and S. S. Zilva[114] is of importance. These investigators grew yeast in a solution of cane sugar, ammonium phosphate, chloride, and mineral salts. All the materials were quite free from traces of vitamin B. *S. ellipsoideus* grew readily in the medium, and the yeast produced was found to contain the vitamin, for it had a curative effect on pigeons suffering from avian polyneuritis. They conclude that yeasts grown on the synthetic medium contain vitamin B, but not in so large a proportion as those grown on wort.

This agrees with the work of E. I. Fulmer, V. E. Nelson, and F. F. Sherwood,[115] and of M. M. MacDonald and E. V. MacCollum,[116] and others who have tested yeast growth in a variety of ways, and conclude that the presence of vitamin B is unnecessary. On the other hand, R. J. Williams[117] estimates the vitamin B content of various foodstuffs by their action on the growth of yeast; S. Fränkel and E. Schwarz[118] use a method in which the accessory factor is estimated by its accelerating effect on yeast fermentation; and C. Funk and H. E. Dubin[119] employ yeast growth for this purpose. It is difficult to reconcile these conflicting views, and more work is required before any vitamin can be confidently estimated by the growth of yeast cells. The value of such a method would be great, and the matter is well worth the attention it is receiving.

A. Harden and S. S. Zilva[120] found no appreciable quantity of

[113] *J. Phys. Chem.*, 1920, **24**, 7?? ; *J. Inst. Brew.*, 1921, **27**, 399.
[114] *Biochem. J.*, 1921, **15**, 438 ; *J.*, 1921, 671A.
[115] *J. Amer. Chem. Soc.*, 1921, **43**, 187 ; *J.*, 1921, 273A.
[116] *J. Biol. Chem.*, 1921, **45**, 307 ; *J.*, 1921, 363A.
[117] *Ibid.*, 1921, **46**, 113 ; *J.*, 1921, 316A.
[118] *Biochem. Zeits.*, 1920, **112**, 203 ; *J.*, 1921, 273A.
[119] *J. Biol. Chem.*, 1920, **44**, 487.
[120] *J. Inst. Brew.*, 1918, **24**, 197 ; *J.*, 1918, 524A.

vitamin B in beer or malt. H. Lüers,[121] however, brings forward evidence to show that dried beer extract prepared from dark Munich beers contains this vitamin. Pigeons fed on polished rice and the dried extract lost weight, but developed no symptoms of polyneuritis. No reference is made in this paper to the one by Harden and Zilva, and it is difficult to say why the two beers give different results.

Bacteriology.

"The Yeasts"[122] is a book of value to those interested in fermentation chemistry, for it contains a description of the characteristics of about 300 yeasts and allied organisms. Each year sees the discovery of more of these organisms, but no indication is forthcoming as to the means by which they come into existence. H. Christoph[123] describes a small wild yeast which causes turbidity in bottled beer. It sporulates, easily forming 2-4 spores per cell. G. de Rossi[124] has investigated the characteristics of two species of apiculated yeasts. These organisms play a part in the initial stages of fermentation in wine-making. They are sensitive to the action of alcohol, and are suppressed in the later part of the fermentation. Some new yeasts (zygosaccharomyces) found on figs are described by G. Chaborski.[125]

A useful account of the properties and classification of lactic organisms is given by P. van Steenberge.[126]. The different species are distinguished by the shape of the organism, the flocculating or non-flocculating character, the maximum and optimum temperature of growth. Some produce only lactic acid, others carbon dioxide, acetic and formic acids, glycerol, and alcohol in addition. Some are harmful to yeast and alcoholic fermentation.

Sugars of a high degree of purity are required for diagnostic purposes in bacteriology. E. H. Eitel[127] describes the progress in the preparation of such sugars in America. Twenty-three different carbohydrates are manufactured commercially and are available for the purpose. E. B. Fred and W. H. Peterson[128] describe the fermentation of sugars (mainly xylose) obtained by digesting maize cobs with sulphuric acid. The organism they use is a bacterium, *Lacto-bacillus pentoaceticus*, which converts the sugar into acetic and lactic acids. The fermentation of a similar medium by *Bacillus acetoethylicum* produced acetone, alcohol, and volatile acids.

[121] *Z. ges. Brauw.*, 1921, 143; *J.*, 1921, 735A.
[122] A. Guilliermond, translated by F. W. Tanner.
[123] *Z. ges. Brauw.*, 1921, 119; *J.*, 1921, 785A.
[124] Through *Brewing Trade Review*, 1921, **35**, 257.
[125] *Ann. de la Brasserie*, 1920, **73**, 90; *Brewing Trade Review*, 1921, 511.
[126] *Ann. Inst. Pasteur*, 1920, **20**, 830; *J. Inst. Brew.*, 1921, **27**, 192.
[127] *J. Ind. Eng. Chem.*, 1920, **12**, 1202.
[128] *Ibid.*, 1921, **13**, 211; *J.*, 1921, 273A.

ACETONE.

The production of butyl alcohol and acetone by the fermentation of starch is a process which continues to receive attention. The hydrolysed starch under the influence of the acetone bacillus undergoes a degradation represented approximately by the equation $3C_6H_{10}O_5 = 2C_4H_{10}O + C_3H_6O + 7CO_2 + 4H_2 + H_2O$. About 35% of the starch is converted into butyl alcohol and acetone Butyric and acetic acids are also produced, and infection of the mash with other bacilli leads to the production of lactic acid. The chemical mechanism of the reaction is discussed by J. Reilly, W. J. Hickinbottom, F. R. Henley, and A. C. Thaysen,[129] and the bacteriology of the process by A. C. Thaysen.[130] G. J. Fowler, Y. D. Wad, and A. G. Gokhale,[131] contribute some notes on the process carried out in India. They find the same difficulty which was experienced at the Royal Naval cordite factory in obtaining complete sterility of the mash. Jawari (cholam) was chosen as the most suitable raw material available. The fermentation plant was made of aluminium.

GLYCEROL.

Progress in the manufacture of glycerol by fermentation consists mainly in studying the conditions to give good yields. A particularly comprehensive account of glycerol from the time of its discovery down to the present day is given by K. Schweizer.[132]

ALCOHOL.

J. Mezzadroli[133] gives an interesting account of the production of alcohol from carobs in a distillery at Catania, Sicily. The fermentation is carried out by special yeasts acclimatised to antiseptics.

The tubers of Jerusalem artichoke contain up to 15% of inulin. This polysaccharide yields lævulose on hydrolysis, and this sugar is valuable. not merely as a sugar but also as a potential source of alcohol. J. J. Willaman[134] considers that the successful extraction is commercially practicable. K. Windisch[135] gives details of the working of this raw material in the distillery. The biochemistry of the Mahua flower has been studied by G. J. Fowler[136] and his collaborators. The dried flowers contain 60–70% of carbohydrates, consisting of dextrose, lævulose, maltose, sucrose, pentoses, and

[129] *Biochem. J.*, 1920, **14**, 227
[130] *J. Inst. Brew.*, 1921, **27**, 527.
[131] *J. Ind. Inst. Sci.*, 1921, **4**, 1; *J.*, 1921, 316A.
[132] *Chim. et Ind.*, 1921, **6**, 149; *J. Inst. Brew.*, 1921, **27**, 559.
[133] *Bull. Assoc. Chim. Sucr.*, 1921, **38**, 510; *J.*, 1921, 786.
[134] *Ann. Brass. et Dist.*, 1921, **19**, 281; *J. Inst. Brew.*, 1921, **27**, 395.
[135] *J.*, 1920, 760A.
[136] *J. Ind. Inst. Sci.*, 1920, **3**, 81; *J.*, 1921, 22A.

cellulose. By fermentation with cultures of yeast naturally occurring in the flower, 90% of the theoretical yield of alcohol was obtained. The flowers were found to be more suitable for the manufacture of industrial alcohol than for the production of acetone.

Many investigations connected with the production of alcohol from cellulose are being carried out at the present time. Sugar cane fibre and cotton seed hulls are shown by E. C. Sherrard and G. W. Blanco[137] to be unsuitable for the purpose, for they yield such a large proportion of pentoses on hydrolysis. A. Wohl and H. Krull[138] obtained from 100 g. of dry pine shavings, 60·9 g. of dextrose estimated by cupric reducing power; this gave 18 g. of alcohol by fermentation. Attempts to produce bigger yields were not successful. G. W. Monier-Williams[139] has succeeded in obtaining crystalline glucose by hydrolysing cotton wool with sulphuric acid. The yield calculated from the analysis of the crude product amounts to more than 90% of the theoretical quantity. No other product of hydrolysis could be detected. This paper is perhaps more of theoretical interest, but it shows the possibility of high yields of alcohol from cellulose.

Wines and Cider.

A. Widmer[140] has investigated fruit wines made from frozen or frost-bitten fruit (apples or pears). Defects appear in the wines, which should be consumed as soon as possible. The harsh flavour of wines made from grapes attacked by insects, according to E. Hugues,[141] is due to the presence of unusually large amounts of acid.

H. Müller-Thurgau and A. Osterwalden[142] describe experiments to show the influence of the ripeness of the fruit on the fermentation of the wines. They also discuss certain maladies of wines and measures of preventing them. Among these may be mentioned the use of pure cultures of yeast, the addition of ammonium chloride as a yeast food, avoidance of high temperatures, and treatment with sulphur dioxide or metabisulphite after fermentation. Judicious blending of juices to ensure the right concentration of tannic acid and acidity is also recommended.

F. Tutin[143] has carefully examined the action of alkalis and pectase on pectin. A salt of pectic acid, acetone, and methyl alcohol are produced in each case. It seems probable that pectin is the isopropenyl ester of pectic acid. The matter is of interest,

137 *J. Ind. Eng. Chem.*, 1920, **12**, 1160; *J.*, 1920, 56A.
138 *Cellulosechemie*, 1921, **2**, 1; *J.*, 1921, 158A.
139 *Chem. Soc. Trans.*, 1921, **119**, 803; *J.*, 1921, 539A.
140 *Chem. Zentr.*, 1921, **92**, II., 878; *J.*, 1921, 445A.
141 *Ann. Falsif.*, 1921, **14**, 139; *J.*, 1921, 557A.
142 *Chem. Zentr.*, 1921, **92**, II., 748; J., 1921, 404A
143 *Biochem. J.*, 1921, **15**, 494.

for wines, cider, perry, and other fermented fruit juices contain pectin which produces traces of methyl alcohol and acetone.

E. Garino-Canina,[144] in discussing the influence of phosphates on alcoholic fermentation, ascribes the failure of certain sparkling wines to condition to the lack of phosphates.

W. Fresenius and L. Grünhut[145] describe methods of detecting some adulterations in wines. Foreign dextro-rotatory substances can be detected by the polarimeter. All the unfermentable constituents of dry wines have a low optical activity; if, therefore, the residue of the wine after fermentation with yeast shows a comparatively high rotation, the addition of some starch syrup can be suspected. Methods of detecting gum arabic and dextrins are also given. A method of determining glycerol in wine is described by A. Heiduschka and F. Englert.[146] The residue of the wine is distilled with boric acid up to a temperature 320° C. The acrolein is distilled into a receiver containing ammonia and estimated by its reducing power on silver nitrate.

Vinegar.

P. Hassack[147] gives an account of vinegar manufacture in the United States. The alcohol necessary for the production is profitably derived from the manufacture of other products such as baker's yeast or de-alcoholised beer. Black strap molasses is the usual raw material of the spirit vinegar manufacturer. The preparation of malt vinegar and cider vinegar is also described. It is interesting to learn that the melon can be used as raw material for vinegar making.

J. Mezzadroli[148] contributes some useful information on acetic organisms. He emphasises the use of pure cultures and advocates pasteurising the beer, cider, etc. before submitting them to the acetic fermentation. Acetic organisms which carry the oxidation too far, and cause loss of acetic acid, can be eliminated by such means.

A. Chaston Chapman,[149] in his description of the manufacture of vinegar in this country, points out the necessity of a further knowledge of the biochemistry of the process.

[144] *J. Inst. Brew.*, 1921, **27**, 323.

[145] *Z. anal. Chem.*, 1921, **60**, 168; *J.*, 1921, 556A.

[146] *Ibid.*, 1921, **60**, 161; *J.*, 1921, 557A.

[147] *Chem. Age*, 1921, **29**, 105 *J. Inst. Brew.*, 1921, **27**, 317.

[148] *Ann. Brass. et Dist.*, 1921, **19**, 195; *J. Inst. Brew.*, 1921, **27**, 181, 481.

[149] Cantor Lecture.

FOODS.

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Food chemistry in its broader aspect touches so many fields of research, commencing with food production on the farm and ending with the influence of diet upon health and disease, that it is not possible in a short review to do more than select certain outstanding features, and indicate the progress which has been made during the past year.

Diet and Nutrition.

In the light of the wider knowledge of nutrition gained during recent years, it is becoming increasingly clear that the purity of individual foodstuffs from the chemical and bacteriological standpoints, and their relative values in terms of calories, are not the only points to be considered in assessing their worth for the purpose of nutrition. In former years the quality of foodstuffs was judged by the extent to which they conformed to an agreed standard of composition, and were free from potentially harmful or actively poisonous ingredients such as might gain access during manufacture, preservation, or distribution. As far as nutritive value was concerned the natural inclination of the consumer, and his freedom of choice, were deemed to be sufficient safeguards.

Civilised man to-day is living under what may be termed artificial conditions as compared with his more primitive ancestors, and his choice of foodstuffs is affected to an ever-increasing extent by factors such as scarcity, cost, difficulties of transport and distribution, etc. These factors all combine to render it difficult for many people to follow their natural inclinations in regard to diet. Furthermore, there is the question as to how far our natural sense of what is good for us may have been dulled or perverted by civilisation, and to what extent our predilections in such matters as appearance, taste, and colour may have undergone a gradual change, in directions opposed to those indicated by considerations of nutritive value.

It is a maxim of the food manufacturer that in the long run the consumer is always right, implying that the foodstuffs most in demand are necessarily those which experience has shown to be the most suited to the needs of the people. This might conceivably be true if man were living in a more or less wild state, under conditions where his survival or non-survival would depend solely upon his

physical fitness, but it can hardly be held to apply to modern conditions of life. While the refined food products of the present day have undoubtedly been evolved from the cruder and more primitive foodstuffs of bygone years by a process of selection on the part of generations of consumers, this selection has followed an artificial rather than a natural course, and the consumer's judgment cannot be relied upon as an infallible guide.

It is now generally recognised that the various dietetic elements are to a great extent interdependent, and the effective utilisation of each foodstuff by the human body depends upon the proper balancing of the constituents. For instance, when carbohydrates are removed from the diet, fats are incompletely oxidised, and it would appear also that the presence of carbohydrates is essential to the normal course of protein metabolism. Certain proteins are found to be inadequate for the maintenance of nitrogenous equilibrium. They are incomplete in respect of their proximate constituents, and possess a low biological value. Again, the presence of unidentified accessory factors, or vitamins, which are assumed, on the evidence available, to be definite chemical substances, has been shown to be essential to growth and to maintenance of health.

There is a danger that too much stress may be laid on the importance of vitamins alone. These factors appear to work in close relationship with the other dietetic elements. While they are undoubtedly essential constituents of any dietary, it does not follow that their presence is all-sufficient. They may be looked upon as links in a chain of dietetic elements, each of which is of fundamental importance in maintaining the continuity of the whole. Or, again, the various dietary constituents may be likened to the several parts of a rotating wheel. Unless the parts be properly balanced, the wheel does not run true. The more varied the diet, the greater the probability that all the necessary constituents are present in sufficient amount. It may be argued that under modern conditions the opportunities of securing a varied diet are greater than they have ever been, and that there is little likelihood, in practice, of appreciable deficiency occurring in any one essential constituent. However this may be, evidence is gradually accumulating which would seem to show that the dietary of large sections of the population, whether owing to acquired taste or to force of circumstances, may be dangerously near to a point at which it is inadequate, not necessarily in quantity, but in quality, for the maintenance of health. "Malnutrition is wider in incidence and more devastating in issue to a community than food-borne disease."[1]

[1] Sir George Newman, *An Outline of the Practice of Preventive Medicine.* *Cmd.* 363, 1919, pp. 65-67.

Proteins.

The present state of our knowledge as to the relative value of the different animal and plant proteins from the nutritive standpoint, has been reviewed by R. H. A. Plimmer.[2] He points out that biologically the proteins must be regarded as mixtures of the various amino-acids, and that the nature and relative proportion of the amino-acids in different proteins vary considerably. Each amino-acid has apparently a definite function to perform in the process of growth and maintenance. If it were possible to obtain sufficient of each individual amino-acid for the preparation of artificial food mixtures, experimental work would be greatly simplified, but the practical difficulties of this procedure are too great. The methods employed are either (1) to feed incomplete proteins and add the missing unit or units, or (2) to feed completely hydrolysed proteins from which one or more of the amino-acids have been removed by chemical means.

An extensive series of researches has been carried out by E. V. McCollum, N. Simmonds, and H. T. Parsons on the biological value of proteins in nutrition.[3] Rats were fed for long periods upon diets which varied as regards the source of the protein, but which were complete in all other respects, and their general health, rate of growth, fertility, and length of life observed. It was found that milk, when forming the only source of protein, was superior to all other foods. Of the cereals, wheat possessed the highest biological value. The proteins of the pulses were, in general, of low value, but animal proteins, especially those from glandular tissues such as kidney and liver, ranked approximately with wheat.

Greater differences were observed in the capacity possessed by different proteins for supplementing each other, and forming mixtures of higher biological value than either of the two proteins separately. Thus the proteins of kidney, liver, and muscle fibre are remarkably effective as supplements for those of cereals, but not to so great an extent for the proteins of pulses. A combination of meat and wheat proteins is of higher biological value than either of the two separately. On the other hand, cereal and vegetable proteins are unable mutually to supplement each other and such mixtures are not of higher biological value than the constituents alone.

One of the essential constituents of proteins from the nutrition standpoint is tryptophane, and several papers have been published recently on the estimation of this substance in various foodstuffs.[4] The methods employed depend for the most part on the red or

[2] *J.*, 1921, 227R.

[3] *J. Biol. Chem.*, 1921, 47, 111, 139, 175, 207, 235.

[4] O. Fürth and F. Lieben, *Biochem. Zeits.*, 1920, **109**, 124; 1921, **116**, 224; *J.*, 1921, 787A.

violet coloration, given by tryptophane with certain aldehydes in the presence of an oxidising agent, and are thus variations of the Hopkins-Cole test, using glyoxylic acid, and of the well-known Hehner test for formaldehyde in milk. O. Fürth and E. Nobel[5] find that casein contains 2·0%, the proteins of cows' milk whey 1·8 to 2·3%, and the proteins of human milk 3·4 to 6·8% of tryptophane.

H. Onslow has studied the conditions under which tryptophane is destroyed in the hydrolysis of caseinogen by acids and alkalis,[6] and gives a detailed account of the preparation of this amino-acid by the digestion of caseinogen with trypsin. The fluid resulting from the digestion is precipitated with mercuric sulphate, the mercury removed by hydrogen sulphide, and the filtrate again digested with trypsin and then extracted with methyl alcohol. In this way yields of 10 to 15 grams of tryptophane were obtained from 1 kg. of caseinogen.

Two new proteins which have been separated from yeast[7] have been found to contain 1·51 and 2·28% respectively of tryptophane. Both proteins also give a high yield of lysine, which is one of the essential amino-acids from the nutrition standpoint, and the high food value of yeast thus receives additional confirmation.

Mention may be made of a paper by H. E. Woodman[8] on the characterisation of different individuals by the method of protein racemisation. When solutions of proteins in dilute sodium hydroxide solution are kept at 37° C., they suffer a progressive diminution in the value of their optical rotatory power. This appears to be due to a keto-enol tautomerism of the: CH.CO. groups in the protein complex. By plotting the diminution in rotation against the time, curves are obtained which are the same for identical proteins, but which differ more or less from each other if the proteins in question differ in amino-acid make-up. The method does not pretend to do more than establish structural identity or non-identity, but it is claimed that for this purpose it is simpler and more rapid than the chemical and biological methods hitherto used. Woodman is able by this method to confirm the identity of the globulins of cow's blood-serum and of colostrum, but finds that lactalbumin and serum-albumin are different in structure. It is well known that colostrum contains a high proportion of lactalbumin and globulin as compared with milk. These two proteins were formerly supposed to pass direct into the colostrum from the blood-stream, without undergoing a separate mammary synthesis, such as occurs in the case of caseinogen. It would seem,

[5] *Biochem. Zeits.*, 1920, **109**, 103.
[6] *Biochem. J.*, 1921, **15**, 383, 392; *J.*, 1921, 672A.
[7] P. Thomas, *Ann. Inst. Pasteur*, 1921, **35**, 43; *J.*, 1921, 234A.
[8] *Biochem. J.*, 1921, **15**, 187.

however, that lactalbumin must also be regarded, in the same way as caseinogen, as a product of mammary synthesis. The high proportion of globulin in colostrum and its transference direct from the blood-stream would appear to be in the nature of an emergency measure during the early days of lactation.[9]

An investigation by G. A. Hartwell on the effect of diet on mammary secretion[10] shows that great differences occur in the initial weight and rate of growth in litters of young rats according to the food of the mother. On diets of bread and milk or bread and meat, both mother and litter did far better than on a basal diet of bread alone. On deficient diets the mother appears to be able to supply certain essential constituents from her own tissues.

Vitamins.

Research work on accessory factors, or vitamins, may conveniently be considered under three headings: (1) their origin and distribution; (2) their stability; and (3) their effects on the animal organism.

It is becoming increasingly clear that the three accessory factors at present recognised, which may be termed, according to Drummond's nomenclature, vitamins A, B, and C, are primarily of vegetable origin and cannot be synthesised by the animal organism. The latter is entirely dependent upon its food for the supply of vitamins necessary for its own development and for that of its offspring in the early stages of growth. The fat-soluble vitamin A appears to be essentially a product of photosynthesis in plants, and its formation under these conditions has been investigated by Coward and Drummond.[11] They found that dried seeds are deficient in this vitamin, and that the quantity is not increased by germination. Plants deficient in chlorophyll, such as etiolated seedlings, white cabbage, mushrooms, etc., are also deficient in vitamin A. On the other hand, it is formed by even the lower chlorophyll-containing plants, such as marine algæ. Red algæ, which are differently adapted for photosynthesis, are not so active in this respect. Vitamin A may be extracted from green leaves by means of fat solvents, and appears not to be associated with the protein complex. These observations lend additional interest to the older work of R. Willstätter and of B. Moore and T. A. Webster upon the constitution of chlorophyll and the mechanism of photosynthesis, and to the researches of E. C. C. Baly, I. M. Heilbron, and

[9] J. C. Drummond, K. H. Coward, and A. F. Watson, *Biochem. J.*, 1921, **15**, 540.

[10] *Biochem. J.*, 1921, **15**, 140.

[11] K. H. Coward and J. C. Drummond, *Biochem. J.*, 1921, **15**, 530; *J.*, 1921, 746A.

W. F. Barker[12] upon photocatalysis, published during the year under review.

Vitamin B appears to occur mainly in the germ or embryo and outer layers of seeds and is also abundant in yeast and egg-yolk. A. Harden and S. S. Zilva[13] find that *Saccharomyces ellipsoideus* is able to produce this vitamin when grown in a synthetic medium in which ammonium salts were the only source of nitrogen.

The antiscorbutic vitamin C is found in the green leaves of plants, especially *Cruciferæ*, and in fresh fruits. It is formed during the process of germination of seeds.

Vitamin A has been shown to be one of the chief factors concerned in promoting normal growth. If further research confirms the fact that it owes its origin to the synthetic processes taking place in plants under the influence of light, it is obvious that here is a fact of fundamental importance from the standpoint of rational diet and nutrition. It is curious that although vitamin A is synthesised by the plant, vegetable oils in general are deficient in this substance. The factor appears to be localised in the chloroplasts and not to be transported, to any great extent, to other parts of the plant. Animal oils and fats on the contrary are usually rich in vitamin A. No hard and fast rule can be drawn in this connexion, but it would seem that the animal organism possesses in high degree the power of storing up this factor in its tissues. A remarkable instance of this is furnished by the cod-fish and other allied fishes. Cod-liver oil, when carefully prepared, is one of the richest known sources of vitamin A. The source of the accessory factor in this case must lie with the green marine algæ, endowed with the power of photosynthesis, which form the ultimate food material of all marine animals.[14]

While the total quantity of vitamin A present in the animal is dependent mainly upon the character of its food, the distribution of the factor in the various organs and secretions appears to be determined by their physiological function. The growth energy of the young is much greater than that of the adult and demands a larger supply of the growth-promoting factor. In the earliest stages of growth this supply can be derived only from the mother. Thus the fat of mammalian milk is richer in this respect than the depôt fat of the body. There is, as it were, a mobilisation of reserves on the part of the mother to meet the needs of her offspring. Colostrum, which is the product of the udder for the first few days after calving, is richer in vitamin A than is normal cows' milk.[15] This

[12] *Chem. Soc. Trans.*, 1921, **119**, 1025; *J.*, 1921, 633A.

[13] *Biochem. J.*, 1921, **15**, 438; *J.*, 1921, 670A.

[14] K. H. Coward and J. C. Drummond, *Biochem. J.*, 1921, **15**, 535.

[15] J. C. Drummond, K. H. Coward, and A. F. Watson, *Biochem. J.*, 1921, **15**, 540; *J.*, 1921, 746A.

selective distribution appears to run parallel with that of the lipochrome pigments which are similarly derived from the green plant and are concentrated in colostrum and also in egg-yolk. This similarity has given rise more than once to the suggestion that these pigments, of which carrotene is the best known, may be intimately connected with the growth-promoting factor, but M. Stephenson[16] has now confirmed the conclusions reached by previous workers that pure carrotene is without action on growth.

Summer and winter milk differ appreciably in vitamin content, the former being the richer in this constituent owing to the fact that in summer cows are fed largely upon grass.[17] The relationship between the food supply and the vitamin content of the body fat has been studied in great detail by J. C. Drummond, J. Golding, S. S. Zilva, and K. H. Coward[18] in connexion with the feeding of pigs. Lard has hitherto been looked upon as an exception to the general rule that animal fats contain more vitamin A than vegetable fats. Lard is a depôt fat, unlike butter which is a product of the mammary gland, but other depôt fats, such as oleo oil, contain this accessory factor in fair quantity. Here again the nature of the food is a controlling factor. The normal diet of fattening pigs contains very little vitamin A, but grass-fed pigs, on the other hand, are able to store up the factor in their tissues, although to a less extent than grass-fed cattle.

A further reason why lard is usually deficient is to be found in the sensitiveness of vitamin A to oxidation at high temperatures. While oleo oil is prepared at as low a temperature as possible, lard is rendered and refined at a high temperature, under conditions which may lead to destruction of the vitamin by oxidation.[19]

This susceptibility to oxidation is also shown in the case of butter, which is inferior in its growth-promoting qualities to the same amount of fat in raw milk. The loss is due mainly to oxidation during working.[20] While butter can be heated to 120° C. for four hours in absence of air without its content of vitamin A being affected, loss of this factor by oxidation may take place at temperatures as low as 37° C.[21]

The importance of vitamin B in the promotion of growth would seem to be at least equal to, if not greater than, that of vitamin A,

[16] *Biochem. J.*, 1920, **14**, 715; *J.*, 1921, 363A.

[17] F. G. Hopkins, *Biochem. J.*, 1920, **14**, 721; *J.*, 1921, 313A. R. A. Dutcher, C. H. Eckles, C. D. Dahle, S. W. Mead, and O. G. Schaefer, *J. Biol. Chem.*, 1920, **45**, 119; *J.*, 1921, 94A.

[18] *Biochem. J.*, 1920, **14**, 742; *J.*, 1921, 363A.

[19] J. C. Drummond, *J.*, 1921, **40**, 81T.

[20] J. C. Drummond, K. H. Coward, and A. F. Watson, *Biochem. J.*, 1921, **15**, 540; *J.*, 1921, 746A.

[21] J. C. Drummond and K. H. Coward, *Biochem. J.*, 1920, **14**, 734; *J.*, 1921, 363A.

but for several reasons a deficiency of the former factor is not so likely to occur, at any rate among the inhabitants of western Europe and America. The water-soluble factor B is more widely distributed than the fat-soluble, especially in pulses and in the whole-meal of cereals, and moreover appears to be more resistant to heat and oxidation. J. M. Johnson and C. W. Hooper[21A] have found that skim milk, when dried by the spray process, retains practically the whole of its vitamin B, as measured by the quantity required to protect pigeons from polyneuritis, and to produce normal growth in rats.

The effect of heat and oxidation on the anti-scorbutic vitamin C is not so well defined and appears to depend to some extent on the particular nature of the foodstuff in question. Although cabbage and other vegetables suffer a loss of 70–80% of their anti-scorbutic potency when dried, fruit juices can be dried with little or no loss. Several papers have been published during the year on this subject[22] and it has been found that commercially dried orange juice retains its anti-scorbutic properties for several months or even years. Milk dried by a spray process is stated to contain less vitamin C than milk dried on steam-heated rollers,[23] while full cream sweetened milk, which is condensed at a low temperature under reduced pressure, has been found to be as effective in this respect as raw milk.[24] The varying susceptibility shown by different anti-scorbutics to heat and desiccation may conceivably be determined by their relative degree of acidity.

One or two interesting points in this question of oxidation may be noted. Vitamin A, while easily destroyed by oxidation, is also apparently destroyed by the hydrogenation of fats and oils. The possibility of oxidation occurring at some point during the refining of oils prior to hardening is, of course, not excluded. It would be of great interest to ascertain whether a crude unrefined fish oil loses its growth-promoting power on hydrogenation alone at a low temperature. Further, there is the question as to whether a fat in which vitamin A has been destroyed by oxidation, can again be rendered active by a process of reduction.

The part played by deficiency of vitamin A in the causation of

[21A] *U. S. Public Health Service, Public Health Reports*, **36**, No. 34, Aug. 26th, 1921.

[22] A. Harden and R. Robison, *Biochem. J.*, 1921, **15**, 521. N. R. Ellis, H. Steenbock, and E. B. Hart, *J. Biol. Chem.*, 1921, **46**, 367; *J.*, 1921, 406A. M. H. Givens and I. G. Macy, *J. Biol. Chem.*, 1921, **46**, 11; *J.*, 1921, 318A. J. F. McClendon, W. S. Bowers, and J. P. Sedgwick, *J. Biol. Chem.*, 1921, **46**, 9; *J.*, 1921, 318A. J. A. Shorten and C. B. Ray, *Biochem. J.*, 1921, **15**, 274; *J.*, 1921, 525A.

[23] H. Jephcott and A. L. Bacharach, *Biochem. J.*, 1921, **15**, 129; *J.*, 1921 525A.

[24] E. M. Hume, *Biochem. J.*, 1921, **15**, 163; *J.*, 1921, 525A.

rickets is still a vexed question. The importance of research in this direction can hardly be overrated, for while scurvy, beri-beri, pellagra, and suchlike diseases are not of frequent occurrence, rickets is a condition which is widespread among civilised communities of the temperate zones, and is "one of the most fertile causes of the crippling and disabling diseases of early childhood."[25]

Mellanby's experiments on puppies indicated that definite rickets could be produced by diets deficient in vitamin A, and that the disease could be prevented or cured by the addition of certain oils and fats to the diet. The oils which produced this effect were those which were known to contain vitamin A. Experiments on other animals, however, have not given such definite results. S. S. Zilva, J. Golding, J. C. Drummond, and K. H. Coward[26] have studied the effect on pigs of a diet rigorously restricted in the fat-soluble factor. Although growth was interfered with and the young died soon after birth and were in several cases malformed, no definite rickets was observed.

A. F. Hess and L. J. Unger,[27] from observations made on groups of infants receiving diets some of which were rich, others deficient in the fat-soluble factor, could not obtain any definite evidence that the rickets which developed in some of their patients could be traced to an accessory factor deficiency.

H. M. M. Mackay[28] fed kittens on a diet deficient in vitamin A, but otherwise adequate, with the result that the animals ceased growing. No evidence of rickets, however, could be established on post-mortem examination.

E. V. McCollum and others[29] have analysed a series of diets on which rats developed rickets, and considered that while the cause could be ascribed in general terms to faulty nutrition (unbalanced diet), it could not be definitely put down to deficiency in vitamin A. They consider that the ratio of calcium to phosphorus in the diet is an important factor in the etiology of rickets. Normal bone formation requires a definite calcium : phosphorus ratio, and if this be upset in either direction rickets may result. The administration of an anti-rachitic substance, such as cod-liver oil, may prevent rickets even when the calcium : phosphorus ratio differs from the normal. One of the functions of vitamin A would seem to be that of assisting the assimilation of calcium and phosphorus where the normal mechanism existing for this purpose has become deranged.

25 Sir George Newman, *loc. cit.*, p. 79.

26 *Biochem. J.*, 1921, **15**, 427.

27 *J. Amer. Med. Assoc.*, 1920, **74**, 217.

28 *Biochem. J.*, 1921, **15**, 19.

29 *J. Biol. Chem.*, 1921, **45**, 343.

On the other hand, L. Findlay, D. N. Paton, and J. S. Sharpe,[29A] as a result of investigations on the calcium balance in healthy and ricketty children, are of opinion that the evidence we possess is opposed to the view that rickets is due to a deficient supply of calcium to the bones. Changes in bones, simulating somewhat those in rickets, can be caused by feeding on a calcium-low diet, but the condition is not that of true rickets. Again D. N. Paton and A. Watson[29B] have found that if scrupulous care be taken as to cleanliness, puppies can be reared free of rickets on a diet of only 0·5 g. of milk-fat per kg. of body-weight, along with bread. They question the view that rickets is a deficiency disease due to a lack of an anti-rachitic factor associated with milk-fat. In young dogs under ordinary laboratory conditions a liberal allowance of milk-fat up to even 14 g. per kg. of body-weight neither prevents the onset of rickets nor cures it when developed. They incline to the view that the total energy intake, together with the conditions under which the dogs are kept, are important factors in controlling the development of rickets. An outbreak of rickets in a kennel of fox-hounds at Adelaide,[29C] in which removal of some of the pups to fresh ground prevented the onset of the disease, suggests that, after all, some bacterial infection may play an important part in the causation of this disease.

That the effect of vitamin A on growth is dependent on the presence of a sufficiency of calcium in the diet is also indicated by the work of A. L. Daniels and R. Loughlin,[30] who have investigated the effect of heat-treatment of milk on the growth of rats. Rats fed on milk pasteurised by a holding process grew at about half the usual rate, and never attained the normal size for adult animals. Rats fed on commercial evaporated milk did not grow and soon died in an emaciated condition but with no signs of xerophthalmia. On sweetened condensed milk growth was normal. The addition of foods rich in both vitamin A and vitamin B did not produce any growth stimulation in the stunted animals fed upon evaporated milk, but when calcium salts, either soluble or in the form of a paste of calcium phosphate in a colloidal medium, were administered growth was stimulated. The authors are of opinion that it is the precipitation of insoluble calcium phosphates during the heating of milk which is responsible for the lowering of its nutritive value. These insoluble salts are to a great extent left behind as a deposit in the pasteuriser or milk container. When special care was taken to include the insoluble material by colloidal suspension

[29A] *Quarterly J. Medicine*, 1921, **14**, 352.
[29B] *Brit. J. Exp. Path.*, 1921, **2**, 75.
[29C] L. B. Bull, *J. Compar. Pathol. and Therap.*, 1918, **31**, 193.
[30] *J. Biol. Chem.*, 1920, **44**, 381; *J.*, 1921, 23A.

results similar to those of normal growth on raw milk were obtained. Sweetened condensed milk, when fed undiluted, is so viscous that the precipitated calcium salts remain in suspension.

One of the conditions associated with rickets in childhood is delayed dentition, which is believed to be a predisposing factor in the causation of dental caries. McCollum[31] refers to some interesting evidence pointing to the possible effect of diet upon the incidence of dental caries. A number of skulls were dug up by Stefansson from a cemetery in Iceland, dating from the ninth to the thirteenth centuries. No carious teeth at all were found in these skulls. The diet of the Icelanders previous to about 1850 consisted of milk, mutton, fish, and fowl, with possibly the eggs of wild birds. The only vegetable food eaten regularly was carrageen moss, but potatoes and turnips were eaten to some extent. The teeth of the natives and their general health were excellent as long as this diet was taken. The deterioration of the teeth apparently began about the time when cereals and sugar were regularly imported into Iceland. The same thing is stated to be true of the North American Eskimo. The statistical data in these matters are bound to be uncertain and incomplete, and it will naturally be suggested that several other factors besides malnutrition may conceivably have been concerned in lowering the physical standard of these races.

In the same series of papers McCollum reviews the general aspect of the nutrition question and the relation of malnutrition to general " unfitness " and industrial fatigue. He advances the theory that the widespread use of cereals, pulses, and potatoes represents an innovation in man's diet and one which is not for the best. McCollum questions the soundness of the view that the cereal grains are the most important and economical sources of human food, in view of the fact that cereal proteins are of low biological value and are unable to supplement one another, and he suggests that the extension of the use of cereals in the diet of man may have already passed the limit of safety.

Different species of animals are found to vary both in their requirements of growth-promoting vitamins and in their relative susceptibility to rickets and scurvy. Pigs, although liable to develop a condition closely resembling rickets, appear to require a very small amount of vitamin A for normal growth and development. Puppies would seem to require a much larger proportion of this factor, while guinea-pigs must have an ample supply of both the growth-promoting and anti-scorbutic factors. The rat can apparently thrive and produce young on a scorbutic diet which will kill the guinea-pig.

[31] E. V. McCollum, N. Simmonds, and H. T. Parsons, *J. Biol. Chem.*, 1921, **47**, 116.

E. M. Hume[32] makes an interesting reference to the possible effect of anti-scorbutic requirements on the geographical distribution of different animals. The need of the guinea-pig for this factor is so large that it has probably limited the creature's geographical distribution, and rendered the numerical success achieved by the rat, mouse, and rabbit in the struggle for existence, an impossibility for it.

From the standpoint of the food analyst it is unfortunate that the characterisation of accessory food factors has not yet passed the stage of animal experiment. The method proposed by R. J. Williams, according to which the growth of yeast in a liquid is a measure of the amount of vitamin B present, has been found to give untrustworthy results.[33] Yeast itself can produce vitamin B when grown on a salt and sugar medium.

No indication of the chemical characters of any of the accessory factors has yet been forthcoming. S. S. Zilva and M. Miura[34] have shown that collodion membranes are permeable to vitamins B and C to much the same extent as to methylene blue, neutral red, and safranine, but of course the diffusing molecule may be either simple or associated. The remarkable work of F. Gowland Hopkins[35] on the isolation from yeast and animal tissues of a crystalline dipeptide, which can behave, according to circumstances, either as a "hydrogen acceptor" or as an "oxygen acceptor," led to the suggestion that this substance might be connected in some way with vitamin B, but on trial the dipeptide was found to have no effect in preventing or curing avian polyneuritis. An interesting observation is made by N. Bezsonoff[36] that only those extracts known to possess anti-scorbutic properties give a blue coloration when tested with a solution of sodium tungstate and phosphomolybdic acid in phosphoric and sulphuric acids. Of the various phenols examined the only one to give this blue colour with the reagent was quinol.

P. Goy[37] claims that he has isolated from yeasts, moulds, and bacteria, a crystalline carbon compound free from nitrogen and phosphorus, which exerts a stimulating effect on the growth of these organisms. This substance exerts its growth-promoting function only after its solution has been heated to 85°–90° C., and

[32] *Biochem. J.*, 1921, **15**, 30: J., 1921, 525A.

[33] R. J. Williams, *J. Biol. Chem.*, 1921, **46**, 113. E. I. Fulmer, V. E. Nelson, and F. F. Sherwood, *J. Amer. Chem. Soc.*, 1921, **43**, 186. W. H. Eddy, H. L. Heft, H. C. Stevenson, and R. Johnson, *J. Biol. Chem.*, 1921, **47** 249.

[34] *Biochem. J.*, 1921, **15**, 422; *J.*, 1921, 671A.

[35] *Biochem. J.*, 1921, **15**, 286.

[36] *Comptes rend.*, 1921, **173**, 466; *J.*, 1921, 747A.

[37] *Comptes rend.*, 1921, **172**, 242.

loses its power at about 168°–170° C. It appears to be distinct from the vitamins A and B of higher plants.

Possibly the material most likely to furnish information as to the nature of vitamin A is the unsaponifiable fraction of cod-liver oil, which has been found by S. S. Zilva and M. Miura to influence the growth of rats in extraordinarily minute doses.[38]

The need for methods by which the nutritive value of foodstuffs may be determined by analysis rather than by the tedious, cumbrous, and relatively inaccurate procedure of animal experiment is emphasised by the claims now being made for proprietary foodstuffs in respect of vitamin content. A case in point is to be found in a patent for the production from wheat bran of an infusion or powder stated to contain water-soluble vitamins.[39]

A general *résumé* of the relation of vitamins to the food supply is given by A. Harden,[40] and a discussion of the whole question of diet in relation to normal nutrition is to be found in a report by J. M. Hamill to the Ministry of Health.[41] Mention must also be made of the valuable series of analysis of different foodstuffs together with their calculated energy values carried out by R. H. A. Plimmer for the War Office, and recently published in book form.[42]

Canned Foods.

Several important papers on the subject of canned foods have recently been published. A comprehensive investigation of the factors influencing heat penetration and sterilisation in canned foods is being conducted by W. D. Bigelow and his collaborators in the Research Laboratory of the National Canners' Association, Washington, D.C.[43] It is well known that high temperatures alone, in the region of 120° to 140° C., are insufficient to kill the spores of the more resistant bacteria. A combination of time and temperature is necessary. Bigelow has determined, for a number of thermophilic organisms isolated from spoiled canned foods, the relationship between temperature and time necessary to effect sterilisation. To take an example, 200,000 spores per c.c. of a

[38] *Biochem. J.*, 1921, **15**, 654.

[39] E. P. 161,238; *J.*, 1921, 406A.

[40] *J.*, 1921, 79R.

[41] Diet in Relation to Normal Nutrition, 1921, H. M. Stationery Office.

[42] "Analyses and Energy Values of Foods," R. H. A. Plimmer. H. M. Stationery Office, 192X.

[43] (1) "Heat Penetration in processing Canned Foods," W. D. Bigelow. G. S. Boshart, A. C. Richardson, and C. D. Ball. *Bull. No.* 16-L., *Research Laboratory, National Canners' Association, Washington, D. C.* August, 1920. (2) "Relation of Processing to the Acidity of Canned Foods," W. D. Bigelow and P. H. Cathcart. *Bull. No.* 17-L. Jan., 1921. (3) "The Thermal Death Point in Relation to Time of Typical Thermophile Organisms," W. D. Bigelow and J. R. Esty, *Journal of Infectious Diseases*, 1920, **27**, 602.

certain strain of a thermophilic organism were destroyed in 1320 minutes at 100° C., 690 minutes at 105° C., 225 minutes at 110° C., 54 minutes at 115° C., 23 minutes at 120° C., 8 minutes at 125° C., 3·5 minutes at 130° C., 1·5 minutes at 135° C., and 1 minute at 140° C.

The time required to destroy all the spores in a suspension of a definite strength is influenced to a considerable degree by the acidity of the liquid. The greater the acidity the less the time required for sterilisation at a given temperature. Bigelow gives data, in terms of p_H values, for the acidity of a large number of foodstuffs, and it is noticeable that the p_H values of all the natural foodstuffs examined are definitely on the acid side of neutrality. For different fruits the p_H values lie, for the most part, between 3·0 and 4·0, for vegetables between 5·0 and 6·0, and for fish between 6·0 and 7·0, although there are, naturally, individual exceptions. The acidity of most foodstuffs is found to increase slightly during "processing," and it is suggested that this may be due to several causes, such as actual formation of acid substances, combination of aldehydic groups, *e.g.*, in sugars, with the amino-groups of proteins, and removal of buffer substances by coagulation and precipitation.

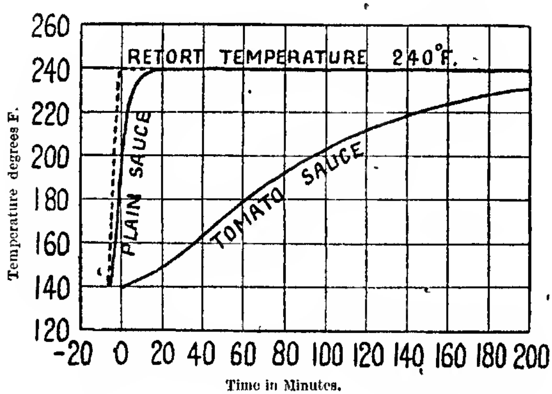
It was further found that the initial concentration of bacteria present influences greatly the time required. The greater the number of spores, the longer must the liquid be exposed to a given temperature to ensure complete sterilisation. Why this should be so is not clear. One would expect that when once the conditions favourable to the destruction of a particular bacterial species had been attained, each individual would be affected to the same degree, however many were present, or, at any rate, that the differences due to normal variation within the species would be inconsiderable. This effect of bacterial concentration has been noted by other observers, and C. Eijkman[44] concluded that it was due to some protective action exerted by substances given off into the medium by the killed bacteria.

Possibly there may be some connexion between this protective action and the hypothetical "X-substance" assumed by T. B. Robertson to exist in bacterial infusions.[44A] He finds that the multiplication of infusoria is accelerated by the addition of a solution in which bacteria have been grown, even though the latter have been killed by heat or removed by filtration, and argues that the effect must be due to the presence of some soluble, non-volatile, thermo-stable product arising from the inhabitation of the medium by bacteria. He further finds that, while single cells of certain infusoria are readily killed by exposure to temperatures above

[44] *Biochem. Zeits.*, 1908, **11**, 12.
[44A] *Biochem. J.*, 1921, **15**, 595.

30° C., cultures containing a large number of individuals will survive continued exposure to considerably higher temperatures.

In the actual "processing" of canned foods by steam-heating under pressure the time taken for the centre of the can to attain retort temperature varies greatly with different foods. Measurements were made with a copper-constantan thermo-couple placed in the centre of the can, which was then processed in the usual manner, and the temperature recorded at regular intervals of time. This method is the same in principle as that adopted by G. E. Thompson in 1919[45] Apart from the size of the can, which is naturally one of the chief factors influencing heat penetration, the nature and consistency of the food are of importance. Heat is transferred from the outside to the centre by convection and conduction. Where the foodstuff consists of fairly large particles surrounded by an aqueous liquor, syrup, or brine, the transfer of heat by convection occurs as quickly as in pure water. Peas and



Rate of heat penetration in "processing" of baked beans in No. 10 cans.

runner beans are typical of this class of product, and heat penetration is comparatively rapid. The presence of starch in solution retards heat penetration until a concentration of about 6% is reached, after which increasing concentration of starch exerts no further influence. It appears probable that other colloids, such as gelatin in meat products, would have the same effect. Foodstuffs which are in a pulpy or finely-divided state, such as spinach or tomatoes, by suppressing convection currents, greatly retard the rate of heat penetration, which then approaches more closely to true conduction. This is strikingly shown in the curves given above which represent

[45] *J. Ind. Eng. Chem.*, 1919, **11**, 657; *J.*, 1919, 651A.

the rates of heat penetration for baked beans in plain sauce and tomato sauce respectively when processed in No. 10 cans.

The theoretical curves for the rate of heat penetration are logarithmic, that is to say the rise of temperature in each short period of time is a constant fraction of the rise in the similar period immediately preceding. The actual rates of heating are found to approach closely the theoretical logarithmic curves. Other factors affecting the time required for processing are the initial temperature of the food and the speed of rotation of the can.

The thermal death time curves for the most resistant bacterial spores are also logarithmic in character. By combining the data for rates of heat penetration with the thermal death time curves, Bigelow deduces "equivalent lethality curves" for each particular foodstuff in cans of a stated size. These curves show the time required for processing the food at different retort temperatures. The canner has thus for each foodstuff a definite range of time and temperature limits which will ensure 100% destruction of bacterial spores, and can select from them that combination which produces the best quality of product, with the assurance of a minimum loss from spoilage.

The above are only a few of the interesting points dealt with in these reports, which should be studied by all who are interested in the manufacture and examination of canned foods of all kinds.

In a special Report to the Food Investigation Board, W. G. Savage[46] deals with the methods used for the inspection of canned foods and their reliability for this purpose. Practically all canned foods with the exception of evaporated milk are packed under more or less of a vacuum. This is effected either by sealing the tins in a vacuum sealing machine, or by passing the filled tins slowly through a steam exhaust box and soldering the vent while the contents are still hot. Sometimes the central hole as well as the cap is soldered in the cold and the tins then put into the retort and given a short heating with steam. After removal from the retorts and while still very hot, the central soldered hole is momentarily opened with a hot iron, and re-soldered when the internal pressure has been relieved. On cooling, the tins should therefore show concave collapsed sides closely pressed against the meat or other contents. The tests employed for the inspection of canned foods before they are passed for consumption, include "palpation" and "percussion." Definitely "blown" or bulging tins, in which there is obvious pressure due to bacterial decomposition, are readily detected by eye, but the less pronounced degrees of spoilage are apparent only by the feel of the tins and by the note emitted when they are tapped with the finger or with a piece of wood. The

[46] "The Methods used for the Inspection of Canned Foods and their Reliability for this Purpose," W. G. Savage, H. M. Stationery Office, 1920.

"palpation" test in the hands of an experienced inspector serves to detect springiness in the tin, that is to say, the vacuum has been lost and the tin is no longer closely adherent to the meat. This loss of vacuum can be due only to access of air or to production of gas. The same defect is indicated by the "percussion" test. If a sound tin be tapped it emits a dull note, but if the tin and the meat be not in contact at any point, the note is tympanitic. A further test is that of shaking the tin, when a characteristic sound is heard if the contents be semi-liquid or "sloppy." Savage subjected to bacteriological examination a large number of canned meats which had been rejected by the trade, or by Food Inspectors of Port Sanitary Authorities, for one or other of the above reasons, and found that in the great majority of cases the contents of the condemned tins were sterile. In other cases the bacteria present were scanty and unimportant and could not be said to have rendered the meat unfit for consumption. While "blown" tins, showing evidence of internal pressure, are definitely unfit for food, it does not follow that tins which have lost their vacuum through minute leaks are unsound, although they may perhaps be classed as potentially unsound. Figures are given in the Report showing the annual wastage of canned meat at the ports, and it is suggested that it might be practicable materially to reduce this wastage by replacing sound meat in tins and re-processing it.

While it is generally accepted that the "blowing" of tins is due to bacterial action, H. Serger[47] considers that in many cases it may be caused by the evolution of hydrogen from the action of acid foods on tin-plate. He gives analyses of the gases found in a number of blown tins containing vegetables. Carbon dioxide and nitrogen were usually predominant, but in certain cases as much as 60% of hydrogen was present. It would seem, however, highly improbable that the presence of hydrogen can be attributed to the action of acids on the tin. If this were so one would expect to find pressure developed in the greater number of canned foods, especially canned fish, which often contains considerable quantities of tin. A. C. Chapman, in 1913,[48] showed that tin was slowly dissolved by tartaric acid in presence of a small quantity of oxygen, with the formation of stannous tartrate, and it is possible that there is sufficient air or dissolved oxygen in most canned foods to account for the solution of tin in this way without evolution of hydrogen.

With modern methods of manufacture and inspection of canned foods the normal loss from spoilage can, by the exercise of constant vigilance and attention, be kept down to 1·5% or less. If inspection be defective, the spoilage may be very high, and it is possible that a certain amount may reach the consumer in a state more or less

[47] *Z. Unters. Nahr. Genussm.*, 1921, **41**, 49.
[48] *Chem. Soc. Trans.*, 1913, **103**, 775.

unfit for consumption. It is important, therefore, to enquire what is the effect on the health of the consumer of food which is in a state of incipient or active decomposition. From experiments carried out on kittens, Savage[49] concludes that, although certain bacteria associated with putrefaction, such as *B. proteus*, are pathogenic when injected under the skin, they appear to be quite harmless when fed to animals. Most of the putrefactive anaerobes, such as *B. sporogenes* and *B. putrificus*, are harmless both when injected and when fed. The evidence as to the toxicity of the so-called "ptomaines" and protein degradation products rests entirely upon injection experiments, and there is no evidence that they have any material toxicity when introduced by the mouth. Food poisoning outbreaks are due to specific food-poisoning bacteria or their specific toxins, and no outbreaks have yet been recorded as originating from the consumption of food in a putrefying condition, unaccompanied by these specific bacteria. At the same time, as Savage points out, it is not safe to assume from experiments on kittens that tainted food is perfectly harmless to man. The animal experiments showed some loss of weight and disturbance of nutrition with the very large doses given, and the intestine of man may be particularly sensitive to such influences. Moreover, if food be found to be decomposed it has evidently been exposed to conditions favouring bacterial infection and such infection may include the specific bacteria associated with food poisoning. Savage cites, as a closely parallel instance of the conflicting views regarding the general and specific causation of disease, the incorrect and exploded hypothesis that bad drains and drain air are the actual cause of diphtheria outbreaks, whereas it is now recognised that such outbreaks originate with an infecting case or contact.

The alleged toxicity of badly blown canned foods has also been investigated by Serger in the paper referred to above. Mice, rats, and rabbits fed on these foods remained in good health in almost all cases.

In a Report to the Ministry of Agriculture and Fisheries on the methods of fish-canning in the British Isles, J. Johnstone[50] reviews the present state of the industry in this country. Although the position of these islands as regards seaboard and access to fishing grounds would seem particularly favourable to the development of a flourishing fish-canning industry, we are apparently far behind foreign countries in this respect. Possibly this is due in some measure to the seasonal distribution of the sprat, which is the ideal fish for a canning industry. British sprats are caught only in the winter and the summer sprat is unknown. In Norway, on the other

[49] *J. Hygiene*, 1921, **20**, 69.

[50] "The Methods of Fish Canning in England," J. Johnstone; *Fishery Investigations*, Series I., Vol. II., No. 1, 1921. H. M. Stationery Office.

hand, the sprat comes into the fiords in the summer and autumn, and when caught at this period of the year is superior in quality to the winter fish. Whether we have here to do with two different types of fish, or whether the British sprat migrates in summer in search of the richer micro-crustacean fauna of the Norwegian fiords, is not clear.

Some interesting analyses are given, showing the seasonal variation in the composition of herrings, sprats, and mackerel. Not only is there a seasonal variation in the amount of protein present, but it would seem that the actual composition of the protein, as indicated by its varying nitrogen content, is subject to seasonal fluctuations. No doubt this is due, in great part, to the annual building up of a considerable mass of highly nitrogenous phosphorised protein into the substance of the ova or spermatozoa.

Still greater variations are found in the proportions of water and fat. An April herring from the Isle of Man may contain as little as 1·7% of fat, while in August the fat content goes up to 29·7%, the water content varying in inverse proportion. In sprats the percentage of water plus fat is nearly constant, being roughly 80·5. The most abrupt change in composition occurs, of course, during the spawning period.

The "maturation" of canned fish is another interesting point discussed in this report. Pilchards, herrings, and sprats preserved in hermetically closed tins must "mature" for at least six months before they attain their best condition as food products. In some cases the process of maturation is said to proceed during five years or longer. The crude and "raw" taste characteristic of the freshly-packed fish disappears on maturation. The bones become friable, the flesh soft and pasty, and the flavour improves very notably. Maturation can hardly be due to the action of intracellular enzymes, which would probably be destroyed at the high temperature of cooking and sterilisation. Moreover, maturation does not appear to be accelerated by keeping the tins at temperatures favourable to enzymic action. It is possible that the effect may be due to the action of thermophilic bacteria, but this would in all probability be accompanied by gas development and blowing of the tins. The suggestion is made that maturation may be due to the catalytic action of the tin dissolved from the inner surface of the can. It is well known that canned fish products often contain an abnormally large amount of tin, the quantity increasing with age until the tin coating is sometimes found to have been completely stripped from the iron.

Johnstone expresses the opinion that British factory methods are, with the exception of the best class of summer-packed East Coast herrings, capable of much improvement. More care is required in the selection of the fish, the mechanical packing, the

quality of the oil employed, and the variety of condiments used. Given the necessary improvement in methods, the British summer or autumn herring is at least as good material for canning as any other fish throughout the world.

In the Report of the Food Investigation Board for 1920 is given a general account of work in progress on the chemical changes occurring in treated and untreated herrings. A method for the determination of trimethylamine has been worked out, based on Foreman's alcohol titration method,[51] and the part played by this substance in determining the quality of herrings is being studied. Concurrently the causes of maturation are being investigated, and it has been ascertained that while the matured product shows a large increase in volatile bases and organic acid radicles, the increase in amino-acids is not so great, indicating that extensive proteolysis does not occur.

Cold Storage.

The importance attached to questions of cold storage of foodstuffs is shown by the fact that of the six Committees organised by the Food Investigation Board no less than four are concerned chiefly with this subject. A Low-Temperature Research Station is being established at Cambridge and should shortly be ready for work. In an interim Report of the Fish Preservation Committee[52] the question of dealing with large gluts of fish is considered. Rapid freezing in cold brine is far preferable to slow freezing in air. The time required for brine freezing is only one-tenth to one-fifteenth of that needed for freezing in air, and there is far less opportunity for differential freezing of the various constituents, with the result that on thawing, the flesh is in practically the same condition as when fresh, no separation of the juices having occurred. In fact, it is stated that the living muscle of a frog is not killed by very rapid freezing. Several points of interest are dealt with in this Report, among them the curious phenomenon of drying in cold store. Although the vapour tension of ice at 0° C. is only 4·6 mm., there is a definite, though slow, evaporation of moisture from the foodstuff. In general, owing to faulty insulation, the temperature of the chamber and of the foodstuff is somewhat higher than that of the freezing pipes. Water vapour will therefore pass continuously from the foodstuff to the pipes, on the surface of which it condenses in ice crystals, so that on prolonged storage the foodstuff becomes almost completely deprived of moisture. This can, of course, be avoided to some extent by glazing the fish or other foodstuff with a thin coating of ice, by freezing it in a solid ice-block, by wrapping each article in glazed paper, or by packing in

[51] F. W. Foreman, *Biochem. J.*, 1921, **14**, 451 ; *J.*, 1920, 613A.

[52] *Food Investigation Board, Special Report*, No. 4. H. M. Stationery Office, 1920.

boxes lined with glazed paper. All these methods mean more or less increased cost and labour, which have to be considered when dealing with a sudden glut. It is clear that one of the ways in which drying may be minimised is by more efficient insulation, and this has been dealt with by the Engineering Committee in a Report to the Food Investigation Board.[53] Their findings, that the heat flow through insulators depends upon the relative preponderance of conduction through the actual solid particles and of convection by means of the intervening air spaces, are strikingly similar to the results obtained by Bigelow for heat penetration in canned foods, referred to above.

In a supplementary note to the Report reference is made to an insulating material consisting of rubber expanded by gas into a highly cellular form. The rubber is prepared by vulcanisation under high gaseous pressure amounting to as much as [illegible]0 atmospheres. The pressure is gradually released during the cooling stage, giving a product permeated with minute gas cells, each enclosed by an unbroken membrane of rubber. The heat conductivity of this material is stated to be lower than that of cork, or of any other substance studied in the course of the investigation.

The freezing of fish is the subject of two patents granted to the Imperial Trust for the Encouragement of Scientific and Industrial Research.[54]

The "black spot" fungus of cold stores, to which reference was made in last year's Annual Report, and which was originally investigated in 1910 by J. M. Hamill and G. Massee, on behalf of the Local Government Board, is the subject of a special Report to the Food Investigation Board.[55] It appears that this fungus grows best on meat at a temperature of 0° C. or just below it. At temperatures slightly above freezing-point bacterial growth on the surface of the meat is usually so vigorous as to inhibit more or less completely the development of the fungus.

Storage of Fruit.

Investigations into the processes which occur during the ripening and preservation of fruit are being conducted by a number of workers. M. W. Onslow's work on oxidases was dealt with in the Annual Reports for 1919 and 1920. She has since examined a large number of plants and fruits for the presence of the catechol-oxygenase system.[56] This system of ferments causes post-mortem changes in flavour and colour, and it is only those fruits which are

[53] *Food Investigation Board, Special Report* No. 5, 1921 (E. Griffiths).

[54] E.P. 154,250 and 154,669; *J.*, 1921, 95A.

[55] *J. Hygiene*, 1912, **12**, 489. *Food Investigation Board, Special Report* No. 6, 1921, F. T. Brooks and M. N. Kidd.

[56] *Biochem. J.*, 1921, **15**, 107, 113.

lacking in the complete system, such as the strawberry and currant, which can be kept in a condition satisfactory for jam-making when frozen in contact with air.

Some remarkable results have been obtained by the "gas" storage of apples.[57] It is well known that fruit on storage continues to respire in much the same way as growing plants, oxidation of the tissues occurring with evolution of carbon dioxide. If the fruit be stored in an atmosphere containing a high concentration (14%) of carbon dioxide, and a correspondingly low proportion (8%) of oxygen, loss of reserve material by respiration is greatly reduced. The apples, moreover, are less susceptible to attack by moulds, and the changes in composition in respect of sugars and pectin are similar to those occurring in cold storage. Gas storage doubles the life of apples as compared with ordinary storage in air.

F. Tutin has found that the pectin of apples when acted upon by alkalis yields sodium pectate, acetone, and methyl alcohol.[58] The action of the enzyme pectase in presence of chalk results in the formation of gelatinous calcium pectate, together with methyl alcohol and acetone. Tutin draws attention to the fact that both methyl alcohol and acetone have been found to be present in cider, being doubtless derived from the pectin of the apple juice, and E. O. von Lippmann[59] attributes the presence of methyl alcohol in rum to the decomposition of pectin derived from the sugar cane. As much as 7·5–8·5% of methyl alcohol was found in three samples of rum.

Acidity of Foodstuffs.

Methods of estimating the acidity of organic mixtures in terms of the actual concentration of hydrogen ions have hitherto been confined in the main to bacteriological and biochemical work. In food analysis it is usual to determine acidity by titration, and to express it either in terms of the amount of standard alkali required for neutralisation to certain indicators, or as a percentage of the particular acid to which the acidity is mainly due. While in many cases this method may still be preferable, there is little doubt that for some purposes a knowledge of the actual concentration of hydrogen ions in the solution is of far greater significance. Two methods can be employed, one depending on the use of the hydrogen electrode and potentiometer, and the other on the employment of a range of indicators so chosen that the colour change of each occurs at a different point in the scale of acidity. The former method possesses the disadvantage of requiring somewhat complicated apparatus and exact observance of delicate manipulative details, while the latter, although admirably adapted for use with

[57] *Report of Food Investigation Board for* 1920, p. 18.

[58] *Biochem. J.*, 1921, **15**, 494; *J.*, 1921, 746A.

[59] *Biochem. Zeits.*, 1920, **106**, 236.

colourless or slightly coloured solutions, is useless when the liquid is very dark. The dialysis indicator method, in which the liquid is dialysed through a collodion membrane against 0·9% sodium chloride, and the p_H value determined, by means of indicators, on the dialysate, would seem to overcome the difficulty with coloured solutions.[60]

N. Evers[61] has given a useful table of indicators adapted for approximate determinations in a commercial laboratory, and the writer[62] has dealt with the practical application of the electrometric method. It will be noted that one of the indicators used by Evers is bromocresol purple, the employment of which in the routine examination of milk samples was referred to in last year's Report. L. Michaelis[63] adopts a different method of working with indicators. He prepares a series of tubes containing varying quantities of *m*- and *p*-nitrophenol and *a*- and *γ*-dinitrophenol, each in a measured quantity of sodium carbonate solution. There is thus available a set of indicators from among which one can be found that gives a medium tint, neither deep yellow nor colourless, when one c.c. of it is added to 6 c.c. of the liquid to be tested. The acidity of the liquid is then found by reference to a table. The range given by this series of indicators is from $p_H=2{\cdot}8$ to $p_H=8{\cdot}4$.

According to W. Ostwald and A. Kuhn[64] the acid taste of a liquid does not depend only upon the hydrogen ion concentration. The extent to which a particular acid causes the swelling of gelatin, and the presence or absence of salts and buffer mixtures have a considerable effect on the acidity as estimated by taste in solutions possessing equivalent hydrogen ion concentrations.

That the intensity of taste of a substance does not necessarily run parallel with the actual amount of it in solution is shown by T. Paul in an investigation of the sweetening power of saccharin and dulcin.[65] Saccharin is usually stated to have a sweetening power 450 times, and dulcin 250 times that of cane sugar. Paul shows that this relationship varies with the concentration. The more dilute the solution the greater is the sweetening power of these substances relative to that of an equal concentration of cane sugar. Thus the sweetening power of saccharin may vary according to concentration from 200 to 700 compared with cane sugar as unity, and that of dulcin from 70 to 350. A mixture of 280 mg. of saccharin and 120 mg. of dulcin in one litre of water has a sweetening power equal to that of 535 mg. of saccharin per litre, although

[60] B. Kramor and C. H. Greene, *J. Biol. Chem.*, 1921, **46**, 42; *J.*, 1921, 317A.

[61] *Analyst*, 1921, **46**, 393; *J.*, 1921, 873A.

[62] *Analyst*, 1921, **46**, 315.

[63] *Woch. Brau.*, 1921, **38**, 107; *J.*, 1921, 490A.

[64] *Kolloid-Zeits.*, 1921, **29**, 266; *J.*, 1921, 867A.

[65] *Chem.-Zeit.*, 1921, **45**, 38, 705; *J.*, 1921, 128A, 601A.

dulcin alone is much less sweet than saccharin. It is of interest to note that, according to S. Furukawa,[66] the sweetest compound known is *a*-antiperillaldoxime, which is 2000 times sweeter than sucrose. This substance is a derivative of perillaldehyde, a constituent of the essential oil of *Perilla Nankinensis.*

L. Grünhut[67] draws attention to the occurrence of lævulinic acid, $CH_3.CO.CH_2.CH_2.COOH$, in many soup extracts prepared from vegetables. Lævulinic acid results, together with formic acid, from the action of mineral acids upon hexose sugars, and is therefore to be found in many foodstuffs if their preparation has involved the use of mineral acids. The method of estimation depends upon oxidation by means of chromic acid to acetic and carbonic acids, the mixture being then distilled and the acetic acid determined by titration. Allowance must be made for formic and acetic acids present as such in the foodstuff, and special precautions are necessary if lactic acid be present, since this acid is also oxidised to acetic acid under the same conditions.

Milk and Dairy Products.

The disposal of whey from cheese factories appears to be a matter of considerable difficulty. According to W. G. Savage[68] there has been a considerable development of milk depôts and factories in the West of England during the last few years. Many of these factories convert the surplus milk of the summer months into cheese, with the result that there is a large quantity of whey to be disposed of. Whey consists of an approximately 5% solution of lactose, together with smaller quantities of lactalbumin, fat, and salts, and on keeping undergoes lactic and butyric fermentation. Obviously the method frequently adopted of running it into streams is open to serious objection. Apparently the quantity which can be disposed of by feeding to pigs is limited by various considerations, and it is not at present remunerative to evaporate whey for recovery of lactose. Apart from the administrative and sanitary questions involved, it seems a pity that such large quantities of potentially valuable material should be wasted, and a method for the economical recovery of lactose or lactic acid from whey would be of great value.

The manufacture of lactose from whey is the subject of two recent patents,[69] in which the precipitation of lactalbumin prior to evaporation is effected by the addition of an alkaline sulphite or thiosulphate. The latter, in presence of the free acid of the whey, gives rise to negatively charged colloidal sulphur, which precipitates the positively charged albumin. In another patent[70] it is suggested

[66] *J. Tokyo Chem. Soc.*, 1920, **41**, 706.

[67] *Z. Unters., Nahr. Genussm.*, 1921, **41**, 261 ; *J.*, 1921, 713A.

[68] *The Medical Officer*, Nov. 5th, 1921.

[69] E.P. 161,887 and 163,937; *J.*, 1921, 403A, 523A.

[70] G.P. 328,782 ; *J.*, 1921, 365A.

that sour whey should be utilised as a feeding stuff by incorporation with straw which has been subjected to alkaline hydrolysis.

The application to milk analysis of methods depending upon osmotic pressure has attracted a number of workers at various times. There is good reason to believe that milk, at the moment of its production in the mammary gland, possesses the same osmotic pressure as that of the blood, from which it is separated in the gland by a semipermeable membrane. The osmotic pressure of mammalian blood-serum is remarkably constant. It has been shown that the osmotic pressure of milk, as measured by the freezing-point, is the least variable of all the analytical and physical data and affords the most accurate means of detecting the fraudulent addition of water. The determination of the freezing-point does not readily lend itself to the routine examination of milk samples, and, moreover, it is useless if lactic acid fermentation has commenced. The osmotic pressure of fresh milk is due mainly to lactose and chlorides, and Mathieu and Ferré's figure, based on the percentage of these two constituents, appears to be widely used in France for the detection of added water.[71] It is doubtful, however, whether this figure takes sufficient account of the complex nature of the soluble constituents of milk, and the information given by it would seem to be little superior, in point of accuracy, to that given by a determination of non-fatty solids.

It might be possible to devise a formula, based on the determination of several of the soluble constituents, which would indicate the amount of added water with a near approach to accuracy, but the analysis would have to include many other substances besides lactose and chlorine.

In connexion with the composition of milk, attention may be drawn to the application to analytical records of the methods used by statisticians, and successfully employed for many years in agricultural research.[72] The variations in the composition of naturally occurring foodstuffs, whether of plant or animal origin, are due primarily to physiological causes and follow more or less closely the regular laws of variation. For most purposes average figures, or ranges of figures, are taken as representing the normal composition of the foodstuff in question, and samples falling outside these limits are classed as abnormal. In the majority of cases they are probably not abnormal, but are a necessary consequence of the laws of normal variation. Unfortunately the correlation of a large number of figures by statistical methods is a laborious proceeding, not to be lightly undertaken, but there is little doubt that the application of such methods to the mass of analytical data, more especially as regards milk, which have now been accumulated,

[71] A. Auguet, *Ann. Falsif.*, 1921, **14**, 204.

[72] G. W. Monier-Williams, *Analyst*, 1920, **45**, 203.

would throw fresh light on the extent of the variations to be expected, and must ultimately be of assistance in determining the causes which lead to such variations.

W. N. Stokoe[73] has published the results of a long series of investigations on the rancidity of butter and margarine fats. He finds that rancidity in these fats is caused almost wholely by the action of micro-organisms. In pure fats the preliminary hydrolysis leading to subsequent oxidation and rancidity is brought about by moisture, air, and light, assisted to some extent by traces of lipoclastic enzymes which have withstood the high temperatures of refining. Micro-organisms are not concerned in the production of rancidity in pure fats, and if introduced into the fat they quickly die, since the fat, being insoluble in water, cannot afford nutriment to the cells. In butter and margarine, however, which contain water and milk solids, the conditions are different, and several of the commoner species of moulds and spore-forming bacteria were found to be concerned in producing various forms of rancidity. Mould spores in fats and oils appear to be very resistant to high temperatures, being able to survive a temperature of 150°–170° C. for several hours, and infection is liable to occur also during subsequent filtration of the oil and working and packing of the margarine.

Egg Powders and Baking Powders.

It might be held at first sight that the terms "egg powder" and "powdered egg" should refer to the same product, but this is by no means the case. Several "egg powders" have been examined by F. F. Beach, F. E. Needs, and E. Russell[74] and it would appear that this name has for many years been applied by the trade to ordinary baking powders coloured yellow. It is only since the recent introduction of dried powdered egg that ambiguity has resulted.

An ingenious method of rendering a baking powder stable to moisture is that of coating the particles of one or both ingredients with a film of solid cellulose acetate or formate. At the baking temperature the cellulose esters are decomposed and the ingredients of the powder can react.[75]

It appears that both lactic and mucic acids are used to some extent as ingredients of baking powders, and a test for lactic acid, depending on the red coloration produced with sulphuric acid and guaiacol, is given by L. Hartwig and R. Sahr.[76]

[73] *J.*, 1921, 75T.

[74] *Analyst*, 1921, 46, 279; *J.*, 1921, 634A.

[75] G.P. 336,665; *J.*, 1921, 599A.

[76] *Chem.-Zeit.*, 1921, 45, 322; *J.*, 1921, 368A.

METALS IN FOODSTUFFS.

Data as to the presence in plant and animal tissues of minute amounts of metals and other elements are always of interest owing to their possible connexion with catalytic or enzymic processes. J. S. Jones and D. E. Bullis[77] find that many of the commonly grown leguminous plants contain manganese, in amount varying from 0·0015 to 0·0140% of the air-dried substance. The largest quantities were found in the leaves. G. Bertrand and M. Rosenblatt[78] find that manganese is present in appreciable quantities in practically all plants. Bradley, in 1907, showed that many fresh-water molluscs contain manganese, which he believed to be derived from certain diatoms capable of absorbing the metal from dilute solution in water. He suggested that this element may possibly be concerned in some way with the respiratory functions. The relationship of manganese and iron to the peroxidases of plants has been discussed by Bayliss in his monograph on the nature of enzyme action.

Zinc is another metal widely distributed in foodstuffs. G. Bertrand and R. Vladesco[79] find it to be present in a number of terrestrial and marine vertebrates, the quantity being at a maximum in the early stages of growth. It is well known that oysters may take up relatively large quantities of zinc, copper, and other metals from solution in water, and traces of these and other elements appear, as pointed out in last year's Report, to be normally present in most plant and animal tissues. The presence of these metals may, of course, be purely adventitious, and in no way connected with metabolic processes. It is possible that many such substances, existing in solution in the soil water, may be drawn up into the sap, and may tend to accumulate in those parts of the plant, such as the leaves, where the greatest amount of evaporation occurs. Any element which is present in the soil may thus be found in vegetable foodstuffs, and eventually in those of animal origin, without being necessarily associated with a definite function in metabolism.

FEEDING-STUFFS.

Work has been continued in Germany on the alkaline digestion of straw, with a view to increasing its feeding value.[80] Although the simpler polysaccharides and carbohydrates present in the straw are, as would be expected, partially destroyed by alkaline hydrolysis, especially under pressure, it is found that the feeding

[77] *J. Ind. Eng. Chem.*, 1921, **13**, 524.

[78] *Comptes rend.*, 1921, **173**, 333; *J.*, 1921, 633A.

[79] *Ibid.*, 1921, **172**, 768; **173**, 176.

[80] *Landw. Versuchs-Stat.*, 1921, **97**, 56; **98**, 1, 43, 129, 249; *J.*, **1921**, 823A.

value of the straw is raised. This is considered to be due to the removal of incrusting materials such as silica and lignin, and to a loosening of the cellulose fibres, whereby they are rendered more susceptible to attack by intestinal bacteria.

E. C. Sherrard and G. W. Blanco[81] describe the preparation of a feeding-stuff by the hydrolysis of sawdust with dilute sulphuric acid under pressure. This method is essentially the same as those which have been employed in the United States for the production of alcohol from wood waste. Although the content of reducing sugars is stated to be raised by this treatment from *nil* to 16% it is probable, according to A. Wohl and K. Blumrich,[82] that when cellulose is treated with dilute acids, the reducing sugars which pass into solution interact, on continued heating, with the residue, and form highly resistant reversion products. These might be less easily digestible than the original cellulose.

G. Laupper[83] puts forward a theory to account for the self-heating of hay in stacks, according to which bacterial action is not concerned in the process. He suggests that moisture is able to activate the oxidases present in dried green hay, with consequent chemical action and evolution of heat. The sequence of reactions assumed to occur is a complicated one, involving the production of ammonia, its oxidation to nitric acid, the action of ammonium nitrate on the carbon of caramelised sugars, and eventually the formation of pyrophoric manganese.

The determination of crude fibre by alternate acid and alkaline hydrolysis, is the subject of an investigation by O Nolte[84] He emphasises the importance of adhering strictly to standard conditions, since the results are greatly influenced by variations in the way in which the hydrolysis is carried out. Even the size of the basin and the rate of boiling affect the results, and the more finely ground the sample the lower is the amount of crude fibre found.

A useful paper by A. Smetham and F. R. Dodd[85] discusses the valuation of feeding-stuffs in terms of their "starch equivalents," and gives analyses of a large number of feeding-stuffs which have come under notice during the last few years.

[81] *J. Ind. Eng. Chem.*, 1921, **13**, 61; *J.*, 1921, 192A.

[82] *Z. angew. Chem.*, 1921, **34**, 17; *J.*, 1921, 158A.

[83] *Landw. Jahrb. Schweiz*, 1920, **34**, 1; *J.*, 1921, 363A.

[84] *Landw. Vers.-Stat.*, 1920, **96**, 326; *J.*, 1921, 57A.

[85] *Royal Lancashire Agricultural Society, Annual Journal*, 1921.

SANITATION AND WATER PURIFICATION.

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During the year under review progress in sanitation and water purification has been considerably hampered by several economic factors. In the early part of the year the high cost of labour and materials was the principal factor; then followed a coal strike lasting for three months, and a period of trade depression which has not yet passed. During the later months of the year, however, acute unemployment led to the formulation by local authorities of proposals to carry out various works for its relief, and among these works many schemes of extension to sewage disposal works and improvement of water supply were included. State financial aid has been available for carrying out such work and the year ended with a period of considerable activity. Scientific progress has not been of a revolutionary character, but has consisted mainly in the accumulation and application of further knowledge of the processes involved in the "activated sludge" or "bio-aeration" method of sewage treatment.

Sanitation.

As in last year's Report, it is proposed under this heading to refer to the treatment of sewage and liquid trade refuse, the prevention of river pollution, the disposal of towns' solid refuse, and disinfectants.

Sewage.

With regard to the well-known processes of sewage treatment on land and by means of artificial biological filters there has been no increase in knowledge during the year. Some local authorities have extended and are extending existing plant, whilst others have held back in view of possible developments of the activated sludge process. In some cases the presence of trade refuse in the sewers has caused considerable difficulty at the sewage works. This has been notably the case in rural districts where the dairy industry has been established and extended, and where whey and milky washings from the factories have been discharged to the sewers. In several instances sewage land has been rendered sick and percolating filters have become sludged up.

In July the Ministry of Health, as a result of preliminary conferences with those interested in the treatment of sewage and trade refuse, issued a circular letter to local authorities, inviting their co-operation in an attempt to keep in close touch with any developments taking place in these subjects. The response has been very satisfactory, and it is the intention of the Ministry to issue interim or annual reports upon the matter, with the concurrence of the local authorities concerned.

It is to be hoped that the opportunity afforded by the drought during the year has been taken by local authorities to make gaugings of the dry weather flow of sewage reaching their sewage disposal works, as the importance of obtaining such gaugings is too frequently overlooked. In the case of manufacturing towns, however, there are two other factors which must have had an influence upon the volume of sewage; these are that, owing to bad trade, the volume of trade refuse has been diminished, and owing to the drought supplies of water have in some cases been curtailed.

The results of investigations which have been carried out in recent years on the activated sludge or bio-aeration method of sewage treatment, are now beginning to be applied on a large scale at various centres, and the Ministry of Health have sanctioned the raising of loans for the purpose of carrying out sewage disposal works on these lines by the Corporations of Reading, Stoke-on-Trent, Rotherham, and Sheffield. There is, however, need for much further experimental work before it can be said that the process is as widely applicable as the percolating filter method of sewage treatment. In the case of ordinary domestic sewages there is now no doubt that it is possible to produce a satisfactory effluent by the process, either by blowing air through or by agitating the mixture of sewage and activated sludge. In the case of sewage containing varying quantities and qualities of trade refuse it is not possible to pronounce an opinion without preliminary experiment in many cases, though the experience at Sheffield, Worcester, and Manchester indicates that certain proportions of waste pickle from metal works, brewery refuse, and dyeworks refuse respectively are without inhibitory effect. Discharges of oil into the sewers have been shown to have an inhibitory effect on the process, both at Sheffield and Manchester, but it is not yet clear whether the oil coats the surfaces of the particles of sludge or whether it forms a thin film on the surface of the liquid, and thus prevents proper oxidation. Probably both factors play a part in the distinct inhibitory effect produced.

It must be said, however, that up to the present no works have been operated on a large scale to deal either with the whole, or a definite proportion of the whole, flow of sewage up to three times the dry-weather flow, though steps in this direction are now being

taken with the unit at Sheffield to which reference was made in last year's report. The preliminary results obtained in working this plant have been given by J. Haworth and F. W. Hodgkinson[1] in a paper read at the Annual General Meeting of the Institution of Municipal and County Engineers. The works at Worcester were described at the same meeting by W. Ransom.[2] Both the Sheffield and Worcester works remained in continuous operation throughout the year, except that the latter were stopped for a short period during the coal strike. After this stoppage the period necessary to bring the works into effective operation again was only some three weeks.

The unit plant installed by W. H. Makepeace at the Tunstall Sewage Works of the Stoke-on-Trent Corporation has also continued to yield satisfactory results, and this Corporation now propose to instal a unit plant at their Hanley Sewage Works in order to relieve the over-taxed existing purification works.

The unit continuous-flow plant installed by E. Ardern at the Davyhulme Sewage Works of the Manchester Corporation has now, after several set-backs, been brought into operation and is working at the rate of three quarters of a million gallons per day. The results will no doubt be published in the forthcoming Annual Report of the Rivers Department of the Corporation, and there is no reason to doubt that they will be satisfactory. The experimental plant constructed by J. D. Watson for the Birmingham, Tame and Rea District Drainage Board, has continued in operation, and much valuable information has been collected, but this has not yet been published.

Several Corporations are now experimenting with a view to testing the applicability of the process to their sewage, and deciding whether remodelling and extensions of their sewage works can be more cheaply carried out on activated sludge lines.

In America the construction of the large plant at Milwaukee to deal with 65 million gallons of sewage per day is proceeding, but otherwise it cannot be said that a great deal of progress has been made in the adoption of the activated sludge process. We owe to H. P. Eddy[3] a very able resumé of the present position of the process in which the theory of the process is dealt with and many inspiring suggestions for further research work are made.

In Canada, especially in the Province of Ontario where electrical power is cheap, very favourable results at comparatively small plants are reported.

A very useful bibliography of the subject, compiled by J. E.

[1] *Surveyor*, July 8, 1921, 29; *Engineering*, 1921, **112**, 86; *J.*, 1921, 559A.

[2] *Surveyor*, July 8, 1921, 41.

[3] *Canadian Engineer*, Sept. 1 and 8, 1921.

Porter and published by the General Filtration Co., Inc., Rochester, N.Y., has reached a second edition during the year.

Scientific contributions to the study of the process have been made by P. Courmont, A. Rochaix, and F. Laupin,[4] and by F. Diénert.[5] These workers conclude that if the action is stopped as soon as the ammoniacal compounds have disappeared from the sewage the percentage reduction of bacteria is very irregular and may amount to only about fifty. A prolonged aeration is necessary to effect a bacterial purification equal to that obtained in percolating filters. They have shown that a period of aeration of six hours is sufficient to remove the cholera vibrion from the sewage, but that this period is not usually sufficient to remove the bacilli of typhus and paratyphus. F. Diénert has investigated the action of phenol on the process and concludes that in the presence of 0·5% the formation of nitrous acid is inhibited, although the ammoniacal compounds are removed. He has also investigated the use of artificial sludge prepared from manganese dioxide, and has proved that in this case the removal of ammonia is a bacterial process and cannot be fully explained on the adsorption hypothesis. In this connexion reference should be made to unpublished researches on the use of fine coal, ferric and ferrous hydroxides, fine sand, and silica gel for the preparation of activated sludges, by J. Haworth, J. H. Garner, and J. Garfield.

It has been shown by F. N. Crawford and E. Barton,[6] by analyses of the air entering and leaving the aeration tank, that only some 10% of the air is used for aeration, and they conclude that the remaining 90% is used for keeping the sludge and sewage in intimate contact by agitation. Results obtained by H. M. Wilson and J. W. H. Johnson[7] support this conclusion.

With regard to the part played by higher organisms in the effective operation of percolating filters H. D. Bell[8] has again drawn attention to the function of *Achorutes viaticus* in maintaining the filtering medium in a clean condition. These organisms apparently feed on the sludge which would otherwise block the surface layers of the filters, and thus enable the filters on which they are present to be used for long periods without renewal.

The problem of de-watering activated sludge to such an extent as to render drying by heat practicable or profitable still remains unsolved, although experiments are still proceeding. A suggestion has been made that the purification process might be operated in

[4] *Comptes rend.*, 1921, **172**, 1696 ; *J.*, 1921, 559A. *Ibid.*, 1921, **173**, 181 ; *J.*, 1921, 600A.

[5] *Ibid.*, 1921, **173**, 184 ; *J.*, 1921, 600A.

[6] *Canadian Engineer*, Sept. 1, 1921, 6 ; *J. Ind. Eng. Chem.*, 1916, **8**, 646.

[7] *Report to West Riding Rivers Board.*

[8] *Surveyor*, Nov. 18, 1921, 345 ; *ibid.*, Nov. 25, 1921, 375.

such a manner as to minimise the production of sludge, but it is not yet clear whether prolonged aeration or agitation would have this effect. As stated last year, preliminary experiments to de-water the sludge by pressing, centrifugal action, or electrical treatment had not proved a success, and further experiments have not been much more promising. It appears that a flat-bottomed settling tank provided with a scraper, such as is used for the de-watering of slimes in the metallurgical industry, is more efficient for the collection of the surplus sludge than a tank with an inverted pyramidal bottom, as it produces a sludge containing a larger percentage of dry matter, but such a sludge is not so readily pumped back into the aeration tank.

With regard to the pressing of acidified activated sludge at Milwaukee some interesting results on the optimum acidity have been published by J. A. Wilson and H. M. Heisig.[9] These authors have shown that the time of pressing is largely influenced by the acidity of the sludge, and that when this is less than $p_H=2 \cdot 6$ or greater than $p_H=4 \cdot 0$ the time of pressing is considerably increased. An optimum acidity of $p_H=3 \cdot 0$ is indicated by the curve obtained on plotting their results in a system or co-ordinates, and the similarity of this curve with that showing the influence of acidity on the swelling of gelatin in water suggests that similar factors operate in both cases. It is not a great step further to suggest that it is the colloidal nature of the sludge which is responsible for the observed effects, and that a study of activated sludge in the light of our incomplete knowledge of the colloidal state of matter is very desirable. In this connexion the three published British Association Reports on Colloid Chemistry have been extended by the Report[10] of a General Discussion on the Physics and Chemistry of Colloids and their bearing on Industrial Questions, held jointly by the Faraday Society and the Physical Society of London. Attention is also drawn to this aspect of the sewage problem by F. W. Mohlman and L. Pearse[11] in a paper on Colloids in Sewage.

Experiments on the de-watering of activated sludge by means of a suction filter constructed of metal gauze are being continued by J. Haworth at Sheffield and E. Ardern at Manchester, and the results so far obtained are very promising. The question of vacuum filtration was very fully discussed at the Filtration Symposium[12] of the 62nd meeting of the American Chemical Society during the year, and the varying types of plant received an adequate criticism.

The utilisation of the manurial value of sewage is still receiving

[9] *J. Ind. Eng. Chem.*, 1921, **13**, 406; *J.*, 1921, 559A.

[10] Published for the Department of Scientific and Industrial Research by H.M. Stationery Office, 1921.

[11] *Surveyor*, Sept. 2, 1921, 154.

[12] *J. Ind. Eng. Chem.*, 1921, **13**, 976 *seq.*

attention, and M. G. Weekes and E. H. Richards[13] have described the straw filter to which reference was made in last year's Report. Filters on these lines are in process of construction for the purpose of producing a substitute for stable manure for use on some of the market gardens which send their produce into London. Apart from sewage farms, this is the only process which attempts to utilise the soluble nitrogenous constituents of sewage. In all other cases it is the sludge or sediment from the sewage which has been utilised as a manure, and ordinary sludge from sedimentation or precipitation tanks only contains about one-fifth of the total nitrogen present in the sewage, and that in a form which is not very readily available as a plant food. In spite of this, however, there has been a very considerable use of such sludge, and local authorities have not generally experienced great difficulty in getting rid of it to farmers, especially if they have de-watered it to the extent which is possible by pressing. Sludge obtained by the settlement of effluents from slate beds or percolating filters, that from the latter being generally termed humus, contains nitrogen in a form which is more readily available as plant food, but not as readily available as the nitrogen present in activated sludge. Further experiments at Rothamsted on the manurial value of this latter form of sludge have confirmed previous results and shown that the value of the sludge can be judged on its nitrogen content, and that the value is equal to that of artificial nitrogenous fertilisers containing the same amount of nitrogen. Recent experiments by E. H. Richards lend support to the theory that the high nitrogen content of activated sludge (as high as 7 or 8%) is due to its abnormally high content of higher organisms, and if such be the case it may well be that these organisms will afford a means of extracting the phosphates and potash from sewage, and thus further increase the manurial value of activated sludge.

In some cases[14] it has been found possible to apply sedimentation sludge in the liquid form to farms by means of a system of distribution pipes, and activated sludge could quite well be applied in the same way in suitable cases.

The whole question of utilising the manurial value of sewage merits much further consideration in view of the continued world shortage of organic manures, and whilst the general adoption of the water-carriage system of sewage disposal has rendered the problem more difficult, the difficulties should not be insurmountable. A study of the Statistical Supplement[15] to the Report of the Nitrogen Products Committee serves to emphasise the importance of the problem.

[13] *Engineering*, 1921, **112**, 86.
[14] *J. Roy. San. Inst.*, 1921, **42**, 90.
[15] *J.*, 1921, 285R.

Besides the utilisation of sewage sludge for its manurial value there are other methods of utilisation which have been suggested or tried. During the coal strike there were many instances in which the air-dried sludge was used directly as a fuel, and in one instance it was only by recovering and using the grease which was discharged from manufactories, and collected on the surface of the settling tanks at the sewage works, that it was possible to maintain the sewage pumps in operation. Attempts have also been made to utilise sewage sludge, mixed with other fuel, in gas producers, but the attempts have not yet led to a successful conclusion.

Some attempts have also been made to mix the sludge with house refuse, and to pulverise the mixture for the production of a fertiliser. The possibilities of this process as a means of utilising the sludge in a comparatively wet condition are deserving of further investigation.

Reference was made last year to the fermentation process, by which the sewage sludge of Birmingham is altered in character and made more readily drainable on drying beds. It was also menisoned that by this process some 30% of the dry solids in the sludge ti gasified. The process has been described by J. D. Watson,[17] who has during the year constructed special tanks at Birmingham in order to collect the gas and utilise it in a gas engine for power purposes.[18] Earlier work on the utilisation of gas produced in septic tanks, and more recent work at Parramatta, Australia, carried out by the Septic Gas Company of Australia, Ltd., led Watson to the idea of utilising the enormous volumes of gas produced in the fermentation of the sludge, and the plant erected at Birmingham is capable of producing sufficient gas from two tons of dry matter in the form of sludge to run a 25 b.h.p. gas engine for six weeks. The process should be capable of wider application, and has not yet been followed even at Birmingham to its extreme limits of economy. It is not known, for example, what is the optimum percentage of moisture in the fermenting sludge or what is the optimum temperature for the bacteria responsible for the fermentation, although the sludge is warmed up by extracting the heat from the exhaust gases of the gas engine. Further, the effect of agitating the sludge, either by circulation by means of pumps, or by blowing the compressed gas through it, on the rate of gas production, has not yet been investigated, although such an investigation is promised.

Liquid Trade Refuse.

During the year under review trade depression has undoubtedly diverted attention from the question of the treatment of liquid

[17] *Engineering*, 1921, **112**, 87.

[18] *Surveyor*, Nov. 13, 1921, 339.

trade refuse, and has, moreover, caused such a diminution in its production that its effect upon the streams into which it is discharged has not been so marked as in former years.

A noteworthy contribution to the question of the bacterial purification of trade wastes has been made by G. McGowan,[19] who has indicated a means of applying the systematic knowledge of the bacterial purification of sewage to various kinds of trade wastes. As chemist to the Royal Commission on Sewage Disposal, he worked out a method of estimating the strength of sewage based upon the amount of oxygen required to oxidise fully the organic matter and ammonia present in the sewage, and found that the ratio of the dissolved oxygen taken up in five days to that required for complete oxidation is, in the case of domestic sewage, about 1 : 3. If a trade waste yields a ratio of, say, 1 : 6 it is oxidised more slowly than domestic sewage on a biological filter, and if such a liquid is diluted or concentrated until the oxygen taken up in five days is the same as that taken up by domestic sewage, the capacity of the biological filter necessary to purify the diluted or concentrated liquid would be twice as great as that necessary for the oxidation of an equal volume of domestic sewage. This is the first attempt which has been made to specify from analytical results the capacity of a biological filter necessary to purify trade wastes. G. P. T. Tatham,[20] from mathematical considerations which he published in a former paper,[21] has shown how the purification of such a liquid depends upon the mean time of contact between the liquid and the medium of the filter, and upon the avidity constant of the liquid. The avidity constant is the numerical measure of the activity of the biological filter, or of the greed of the liquid for oxygen, and can only be estimated on the assumption that the oxidation of the liquid follows the same law as a chemical reaction of the first order. In applying this theory to the experimental results published by McGowan, Tatham is able to indicate the capacity of filter required to effect a given percentage of purification.

The Ministry of Health have decided to make special provision for keeping in closer touch with experimental investigations which are in progress on the treatment of trade refuse, and in July a circular was issued, inviting the co-operation of local authorities and others interested in the matter. It is to be regretted that no provision is made for the initiation of experiments by the Ministry on the lines of those undertaken by the Landesanstalt für Hygiene in Berlin and by the Public Health Service of the United States of America. This service has undertaken a series of studies on the treatment and disposal of industrial wastes under the supervision

[19] *J.*, 1921, 148T.
[20] *J.*, 1921, 201T.
[21] *J.*, 1916, 711.

of E. B. Phelps, and Public Health Bulletins[22] have been issued by the U.S. Government Printing Department, giving the results obtained with strawboard waste, tannery wastes, and creamery wastes.

Bulletin No. 109 is of special interest, owing to the fact that in this country the nuisance caused by the discharge of the refuse from milk and cheese factories, both into sewers and into streams, is increasing, and the American investigators show that it is quite practicable to treat these discharges by the methods ordinarily available for the treatment of sewage. W. G. Savage[23] has drawn attention to the importance of the problem in Somersetshire. He estimates that the whey discharged from cheese factories requires more than a hundred times as much oxygen for its oxidation as ordinary sewage, and is of the opinion that the whey should be utilised instead of being discharged into the streams. The lactose factory erected by the Ministry of Agriculture and Fisheries for the purpose of demonstrating the possibility of making lactose from whey in this country, to which reference was made in last year's Report, has been brought into operation, but the results of its working have not yet been published.

In Pennsylvania the treatment of acid waters containing iron has received attention by L. D. Tracy.[24] He gives an analysis of the mine water from Calumet mine, showing an acidity due to sulphuric acid of 21·3 grains per U.S. gallon, 5·5 grains of ferrous sulphate, 59·3 grains of ferric sulphate, and 26·6 grains of oxides of iron and alumina in suspension. The effect of such water, if used for condensing purposes at a large electric power station, can readily be imagined, and its use for coke quenching would discolour the coke and increase its sulphur content. It was therefore necessary to treat it before use. The water was mixed with ground limestone, which neutralised the acidity and reacted with the ferric sulphate to form ferric hydroxide. To separate the precipitate, ferric hydroxide containing a little calcium sulphate, a Dorr thickener was employed, and the thickened precipitate was dried and sold for use in the purification of gas. The volume of water pumped from this mine is a million gallons a day. The paper also contains analyses of other mine waters, showing acidities up to 366·2 parts of sulphuric acid per 100,000 and total iron content up to 111·2 parts per 100,000. Similar acid and ochre waters are to be found in the valleys of the Don and Loxley, near Sheffield, and analyses of these waters have been published by J. Haworth and J. Evans,[25] and the acid waters from the Rand mines in South Africa have been dealt with by F. W. Watson and R. A. Cooper.[26]

[22] No. 97, Oct., 1918; No. 100, Nov., 1919; No. 109, Nov., 1920.

[23] *The Medical Officer*, Nov. 5, 1921, 197.

[24] *Trans. Amer. Inst. Min. Met. Eng.*, 1920.

[25] *J.*, 1920, 394R; 1921, 91T.

[26] *J. Chem. Met. Soc. S. Africa*, 1921, **22**, 30; *J.*, 1921, 853A.

The recovery of zinc and copper from the acid liquors in which these metals have been pickled has been described by W. W. Skinner and J. W. Sale.[27] From liquid refuse, which amounted in volume to 5400 gallons per hour and contained 9 lb. of copper, the metals are profitably recovered by an electrolytic method at the Bridgeport Brass Works, Conn., U.S.A.

The recovery of ferrous sulphate from waste sulphuric acid pickling liquors has long been practised, but attempts to recover any valuable product from hydrochloric acid pickling liquors have only hitherto met with partial success. During the year E. V. Chambers has erected a plant in which such waste liquors are treated with sulphuric acid for the recovery of the hydrochloric acid, so that it may be re-used.

A new process of coal washing by means of froth flotation, which is being introduced in the South Wales coalfield and in North Yorkshire, may render coal washing waste more difficult to treat. The process has been described by F. B. Jones,[28] and by E. Bury[29] and others. As the frothing agent is usually an oil such as cresol or paraffin oil, there is a danger of some of this being contained in the coal-washing liquid refuse and rendering the settlement of the suspended matter more difficult.

The subject of the disposal of waste liquors from the legal and administrative standpoints was very ably dealt with by E. Ardern[30] in the Chairman's address to the Manchester Section of the Society in October. He urged manufacturers to treat the disposal of waste liquids as an integral portion of their manufacturing processes, ranking in importance with such matters as water supply and transport facilities, and pointed out that a closer study of the nature of waste liquids will assist materially in the efficient control of the manufacturing process itself.

It may well be pointed out that had not a period of trade depression, and consequent non-user of water for manufacturing purposes, occurred during the drought of the past year many manufacturers would have been without a sufficient supply of water, for on public health grounds domestic supplies must take precedence over supplies for trade purposes. In such circumstances the manufacturer would be well advised to have at hand a reserve supply in his liquid trade refuse, which he can purify and often use over and over again.

River Pollution.

The year under review has shown an increasing tendency on the part of local authorities and those associated with fishing interests,

[27] *J. Franklin Inst.*, 1921, **192**, 785.

[28] *Proc. S. Wales Inst. Eng.*, 1921, **37**, 331 ; *J.*, 1921, 758A.

[29] *Trans. Inst. Min. Eng.*, **60**, 243 ; *J.*, 1921, 835A.

[30] *J.*, 1921, 462R.

to bring back the state of our more polluted rivers to that which existed before the war. Both local Sanitary Authorities and Fishery Boards have been more active in their attempts to administer the Rivers Pollution Prevention Acts and the Salmon Fisheries Act respectively, in spite of the fact that these Acts are sorely in need of amendment in the light of the labours of the Royal Commission on Sewage Disposal. The difficulties met in the administration of the former Act have been described by E. Ardern[30] in the paper already mentioned. A Bill to amend the Salmon and Freshwater Fisheries Acts was introduced into Parliament as the Salmon and Freshwater Fisheries Bill by the Minister of Agriculture and Fisheries, but had to be withdrawn in August. The Bill contained clauses dealing with river pollution, and strengthened similar clauses in the older Act in that it prohibited the discharge of liquids which would render the water injurious to fish or the spawn of fish, whereas the older Act required fish to be killed before a Fishery Board could take effective legal action. It also gave to Fishery Boards the power to take proceedings under the Rivers Pollution Prevention Act, 1876. It is to be hoped that the Bill may be shortly re-introduced in the interests of our freshwater fisheries, or that some amendment of the Rivers Pollution Prevention Acts may be made.

The Minister of Agriculture and Fisheries has recently appointed a small Committee[31] to assist in dealing with the question of river pollution, on which Fishery Boards, Angling Associations, and the Federation of British Industries are represented. The main function of the Committee is to assist the Ministry in the investigation of pollutions, and of their effects upon fish life, and of the means by which pollutions may be controlled or avoided, and to educate public opinion in the matter. Such a Committee should be capable of very useful work.

The Committee which was appointed in May, 1919, jointly by the Ministry of Transport and the Ministry of Agriculture and Fisheries to investigate the effect upon fisheries of washings from tarred roads has not yet finished its labours, but from the investigations which have been carried out the following tentative conclusions[32] have been drawn :—

(1) That rain washings from a water-bound macadam road surface are not in any ordinary circumstances injurious to fish or fish food.

(2) That the first rain washings from a road surface which has been recently tarred (say, within a week) will certainly be injurious to fish and fish food unless mixed with at least an equal volume of clean water, and may be injurious unless mixed with a considerably

[31] *Yorkshire Post*, Dec. 21, 1921.

[32] *J. Inst. Municipal and County Eng.*, Nov. 5, 1921, IX.

larger volume of clean water. That they will not, however, be injurious to fish or fish food if diluted with at least ten times their volume of clean water.

(3) That subsequent rain washings from a tarred road in the early stages of its life are not injurious to fish and fish food provided they are mixed with at least an equal volume of clean water.

(4) That filtration through freshly-cut turf reduces, to an extent not yet precisely ascertained, the injurious character of rain washings from a tarred road.

(5) That storage of rain washings from a tarred road reduces in some respects their toxic character.

(6) That there is no evidence that pond vegetation is injured by rain washings from a tarred road.

The conclusions are based upon observations taken at the Alresford Experimental Station in Hampshire during the first six weeks after tarring, and may be applicable only to waters similar to the chalk waters of the Upper Itchen. Further observations are to be taken.

In the Midlands there has arisen a feeling that all is not well with the condition of the River Tame and its tributaries above Birmingham, and recent Conferences[33] amongst the local authorities concerned may lead to the formation of a Joint Authority to take the necessary steps to abate existing and prevent further pollution. The River Trent at Nottingham is rapidly becoming seriously polluted owing to manufacturing operations and the discharge of improperly purified sewage in its upper reaches, and the River Tame is a contributory factor to this pollution.

Mention has already been made of the treatment of water pumped from mines. Such water, if discharged in the state in which it is raised from the mine, is exempt from the provisions of the Rivers Pollution Prevention Act, and owing to the damage caused by such water in Lanarkshire the County Council have urged the introduction of legislation to deal with the matter.

Probably the most serious source of pollution during the year has been the refuse discharged from dairies and cheese factories,[34] and complaints have been made of pollution from flax retting. The milk sugar or lactose contained in the whey, which often is, but should not be, discharged with the floor swillings and can washings of the milk factory, forms an excellent food for organisms. Some work on the subject has been done by Thresh and Beale,[35] who have indicated the possibility of destroying the lactose by fermentation with pig's dung or cow dung.

Towards the end of the year the Water Power Resources Committee appointed by the Board of Trade in June, 1918, issued their

[33] *Surveyor*, Jan. 20, 1922, 47.

[34] *The Medical Officer*, Nov. 5, 1921, 197.

[35] *Mun. Eng. and San. Rec.*, Nov. 24, 1921, 548.

Final Report,[36] in which they recommend the setting-up of a controlling Water Commission for England and Wales. Among the powers and duties of this Commission would be the adjustment of conflicting interests in connexion with the use of water for any particular purpose, the grouping of the watersheds of the country into suitable areas, and arranging for the setting-up of Watershed Boards in substitution for the large number of various local authorities now concerned with different interests. The Committee are in general agreement with the recommendations of the Royal Commission on Sewage Disposal and they make specific recommendations in paragraphs 309 and 310 of their Report for the establishment of the proposed Watershed Boards and for extending the scope of the Rivers Pollution Prevention Acts.

Under present financial conditions no doubt the recommendations set out in the reservation to the Report and in the separate Report signed by one member of the Committee will be more in accord with public opinion. In these it is suggested that the proposed Commission is not necessary, as it would lead to the duplication of much work already performed by existing Government Departments.

Towns' Solid Refuse.

The enormous expenditure incurred in the collection and disposal of household refuse is not generally realised, but when it is stated that on the average one-eighth of a local authority's expenditure is incurred for these purposes the importance of the matter becomes apparent.

The recent publication, more especially in America, of literature dealing with the character, collection, and disposal of municipal wastes serves to indicate the increasing importance attached to the subject. Deserving of special mention are the publications of the U.S. Public Health Service by H. R. Crohurst.[37] and of R. Hering and S. A. Greeley.[38] In this country J. A. Priestley,[39] of Sheffield, has drawn further attention to the fuel content of domestic refuse. He estimates that the ten million tons of house refuse produced annually in Great Britain contains three million tons of fuel, having a calorific value of about 10,000 B. Th. U. per lb., which can be separated by screening. The fine dust in the refuse amounts to 40 or 45% of the whole and this has been shown to have considerable value. The salvage plant at Sheffield for dealing with municipal wastes is a model of its kind, and is being extended on a considerable scale.

[36] H.M. Stationery Office, 1921.

[37] *Public Health Bulletin No.* 107, Oct., 1920, U.S. Government Printing Office, Washington.

[38] McGraw Hill Publishing Co., New York, 1921.

[39] *Surveyor,* June 17, 1921, 434.

During the year many complaints have been made against the practice of dumping household refuse, and this may be taken as an indication of the fact that public opinion is being educated in the practicability of other methods of disposal. Local conditions vary from place to place to such an extent that it is not practicable to apply the same method to every case. In one case utilisation will have its advantages, in another pulverisation, and in others incineration may be the best suited. Again, a combination of these methods may be applicable.

The reduction of house refuse by pulverisation is undoubtedly a step forward on the practice of dumping, and farmers are appreciative of the mechanical and fertilising value of the pulverised material, especially on heavy land.

The problem of the disposal of the house refuse of London, much of which is dumped in the adjacent districts, has received the attention of a Conference [40] of the Metropolitan Boroughs during the year, and it is to be hoped that the experience of some of the boroughs such as Southwark and Marylebone,[41] may prove of benefit to others.

The possibility of mixing pulverised house refuse with sewage sludge and the use of the mixture as a fertiliser, deserves further attention, as the dry pulverised material would appear to afford an absorbent for the moisture present in sewage sludge.

Disinfectants.

Under this heading there is little advance to report during the year under review.

Our knowledge of the subject has been brought up to date by the publication of S. and E. K. Rideal,[42] on "Chemical Disinfection and Sterilisation," and the value of chloramine [43] as a germicide has received some attention.

There is need for a good deal of research work on the disinfecting value of organic chemicals, their germicidal effect on specific organisms, and the influence of specific groupings of the constituent elements in the molecule. The effect of the position of such groupings in the molecule is also worthy of further study. The result of such research work would be to place in the hands of chemical manufacturers the possibility of producing a range of disinfectants comparable with the range of dyes now available.

WATER SUPPLY.

With regard to the supply of water for domestic purposes the outstanding features of the year have been the prolonged drought

[40] *Ibid.*, Jan. 6, 1922, 6.

[41] *J. Roy. San. Inst.*, 1922, **42**, 251; *Surveyor*, June 24, 1921, 464.

[42] Ed. Arnold, London, 1921.

[43] *Chem. Trade J.*, Nov. 26, 1921, 667.

and the effects produced by it. The yield of the sources of water supply has been low, not only on account of the abnormally low rainfall, which on the average can hardly have exceeded 50% of the normal, but also on account of the excessive evaporation and consequently low percentage of percolation. It is perhaps yet too early to gauge the full effect of the drought, but attention was drawn to various possibilities in a circular [44] issued by the Ministry of Health in September, and the Ministry are collecting information on the subject in connexion with the survey of the water resources of the country which is being carried out at the present time. The importance of the subject has been ably expounded in two special articles [45] in the *Lancet*. In this circular the attention of local authorities and others concerned with the supply of water was called to the necessity for vigilance in all cases. A prolonged drought increases the risk of the occurrence of water-borne disease in many ways, and the prevalence of epidemics, particularly cholera, in some foreign countries has been a cause of anxiety to those who are responsible for the public health. The danger of an increase in the plumbosolvent action of water derived from a peaty source must also be borne in mind. Apart altogether from the inconvenience of a shortage of water, the drought has rendered supplies which are at all liable to pollution less safe by reason of the fact that the concentration of the pollution has been increased, and in the case of deep-seated sources of supply the liability to pollution has been rendered possible by reason of cracks in the surroundings. The best methods of dealing promptly with drinking water which has become polluted, or which is suspected of spreading disease, are by boiling or by chlorination. It is to the latter method that the larger Water Authorities will have recourse, and during the year much progress has been made in its adoption. The process of chlorination was described as fully as practicable in an appendix to the above circular, and methods for removing the taste from chlorinated water were described.

Chlorination can be effected by the use of chloride of lime (bleaching powder), sodium hypochlorite, "chloros," or liquid or gaseous chlorine. The continued chlorination of the London water supply is dealt with by Sir A. C. Houston in his Fifteenth Annual Report to the Metropolitan Water Board, and the example set by the Board in adopting chlorination in 1916 is already producing effects, in that it is being followed by other Water Authorities in this country as an additional safeguard against water-borne disease.

In America, as stated last year, the process has been extensively adopted, and without chlorination most supplies from the Great Lakes [45] cannot be considered safe. It is very desirable that those

[44] *Circular* 241, Sept. 15, 1921.
[45] *Lancet*, Aug. 13, 1921, 353; Jan. 21, 1922, 145, 148.

responsible for the chlorination of supplies in this country should follow the example of their American colleagues and publish their experience. It may be that in this country prejudice against any chemical treatment of water dies hard, and if it were generally known how many of our water supplies are treated with coagulants and chlorine there would be a public outcry. However, the advantages to be gained by publication and pooling of results far outweigh the disadvantage of any such outcry, and moreover, publication would serve to educate public opinion. In this connexion reference should be made to articles on water storage and sterilisation by G. A. Johnson,[47] and on some problems in water chlorination.[48]

H. Konrich[49] has described experiences in connexion with the water supply to the German armies in the field, and Belgian experience has been described by A. J. J. Vandervelde.[50]

As a result of the water shortage Water Authorities will have to take steps to conserve their supplies of pure water, or to seek additional supplies from sources which under normal conditions would not be considered safe. Such supplies may often be rendered safe by adequate treatment. For the conservation of existing pure supplies, the prevention of waste, the use of less water without risk of injury to health, the intermittent supply of water, and the substitution of less pure supplies for the purer supplies for manufacturing operations and other non-domestic purposes, may all be practised. Perhaps the most notable example of the last type of conservation is furnished by Sheffield, where compensation water from one of the supply reservoirs has been partially replaced by treated river water abstracted below the town and pumped back to a storage reservoir at the foot of the supply reservoir. The project, to which reference has been made in the two last Annual Reports, was brought into operation during the year, but unfortunately the storage reservoir has recently burst[51] and some three million gallons of water flooded the valley.

The control and operation of water purification plants has been dealt with in the second edition of a treatise on the subject by M. F. Stein,[52] and by correspondence[53] arising upon a review of this book, and a rapid method of chlorination control has been worked out by A. Wolman.[54] He advocates the estimation of the chlorine

[46] *Eng. News Rec.*, Mar. 24, 1921, 492.

[47] *Canadian Engineer*, June 23, 1921; *Proc. Amer. Waterworks Assoc.*, July, 1921.

[48] *Eng. News Rec.*, Sept. 8, 1921.

[49] *Gesundheits-Ingenieur*, 1920, **43**, 503.

[50] *Bull. Soc. Chim. Belg.*, 1921, **30**, 119.

[51] *Mun. Eng.*, Jan. 26, 1922, 89.

[52] Chapman and Hall, London and New York.

[53] *J.*, 1921, 159R, 215R, 291R.

[54] *Eng. News Rec.*, Apr. 14, 1921, 639.

absorbed by the water in five minutes and the addition of 0·2 part per million in excess of this amount. It may be noted here that in American practice much larger quantities of chlorine are used than in English practice. Studies of the hydrogen-ion concentration in natural waters have been made by A. Wolman and F. Hannon,[55] and these will have a distinct bearing upon the effectiveness of chlorine treatment, according to the work of E. K. Rideal and U. R. Evans [56] on the effect of alkalinity on the use of hypochlorites, and also upon the action of the waters on pipes and fittings. American standards for the quality of water form the subject of a contribution by J. J. Hinman, Jr.,[57] and a new edition of *Standard Methods of Water Analysis* has been published by the American Public Health Association.

Reference was made last year to the possibility of several Local Authorities combining in order to lessen the per capita cost of providing a pure water supply. Such combinations have been effected in South Wales by the passage during the year of such legislation as the Taf Fechan Water Supply Act and the Rhymney Valley Water Act. The principle underlying these combinations should be applicable with advantage in many other districts.

The study of the biology of waterworks merits more attention than it has received in the past. A considerable amount of disconnected work has been carried out, especially in Germany, but the absence of a modern systematic treatise on the subject is to be deplored. Such works as *Die Mikroskopische Wasseranalyse* (Mez) *Die Mitteilungen aus der Landesanstalt für Wasserhygiene zu Berlin*, *The Microscopy of Drinking Water* (Whipple), and *The Biology of Waterworks* (Kirkpatrick. British Museum. Economic Series No. 7. 1917) deal with special aspects of the problem. The latter publication affords very useful information upon the biological aspect of incrustation. It would appear that corrosion and incrustation have caused considerable trouble, perhaps more in America than in this country, and experience in Kansas City, Missouri, has been described by C. S. Foreman.[58] The subject has also been dealt with by W. H. Walker and D. Ellis [59] and by W. Ransom.[60]

The biology of waterworks includes not only bacteria but the higher plants and animals which occur in reservoirs and grow in the watermains, on filters, and even, as shown by Houston, on the leather washers of taps. These organisms have been studied by Houston and much information on the subject is to be found in his

[55] *Chem. and Met. Eng.*, 1921, **25**, 502.

[56] *J.*, 1921, 64R.

[57] *J.*, 1921, 325R.

[58] *Proc. Amer. Waterworks Assoc.*, July, 1921.

[59] *Mun. Eng.*, Jan. 26, 1922, 78.

[60] *Surveyor*, Nov. 25, 1921, 371 ; *J. Mun. and County Eng.*, 1921, **48**, 408

reports to the Metropolitan Water Board. Some give rise to specific tastes in the water and experience at Marquette, Michigan, has been described by W. C. Brockway.[61] Others are dependent upon the presence of iron in the water, others again on the presence of manganese, and all are dependent upon a suitable food supply, Experiences with iron in the public water supply at Shelby, Ohio, are dealt with by P. Burgess.[62] Algal growths in a reservoir at Birmingham[63] were a source of trouble in 1920, and G. F. Gilkison[64] has recommended the painting of the reservoir walls with a solution of copper sulphate in order to prevent such growths.

Filtration is often sufficient to remove both the organisms and their food from the water, but the value of chlorination for the purpose of preventing the growths should not be lost sight of. A study of the organisms in water surviving chlorine treatment has been made by M. A. Sheeton,[65] who concludes that *B. Welchii* or *B. enteritidis sporogenes* may survive. Houston[66] has contributed to the same subject.

It is yet too early to form an opinion upon the effect of using concrete and reinforced concrete[67] water mains and to say whether the growth of organisms in such mains will be greater or less than in iron mains. The reduced capacity of water mains, due to effects which are generally only very imperfectly examined, is very variable with different waters as the following table [68] shows :—

District.	Diameter of main, inches.	Period in use, years.	Reduction in carrying capacity. %
London	30	110	Nil.
Birmingham	42	15	25
Liverpool	42	8	25
Manchester	44	20	40

A very useful contribution to our knowledge of the nature and removal of colour in water has been made by J. Race.[69]

The softening and purification of water for use in industrial operations scarcely comes within the scope of the present article, but as already indicated the problems under this heading will

[61] *Eng. News Rec.*, July 14, 1921.

[62] *Proc. Amer. Waterworks Assoc.*, May, 1921; *Mun. Eng.*, Nov. 10, 1921, 476.

[63] *Mun. Eng.*, May 5, 1921, 386.

[64] *Surveyor*, Jan. 7, 1921, 4.

[65] *Eng. News Rec.*, June 21, 1921, 929.

[66] *Ibid.*, Sept. 22, 1921.

[67] *Surveyor*, July 29, 1921, 81.

[68] *Mun. Eng.*, July 28, 1921, 88.

[69] *J.*, 1921, 159T.

become of increasing importance as our sources of supply become used up, and as long as the need for financial economy continues. Many manufacturers would find it less expensive to use and treat a hard and impure water readily available than to purchase a supply brought by the Local Water Authority from a distant source.

The subject of water supply has been dealt with by the Water Power Committee[70] of the Conjoint Board of Scientific Studies, who have urged that Imperial resources should be explored, and by the Water Power Resources Committee[71] appointed by the Board of Trade in June, 1918. This latter Committee's recommendations have already been discussed under the heading of River Pollution.

Reference should be made by all those who are interested in waterworks and water purification and supply, to the admirable official circular issued quarterly by the British Waterworks Association, for therein will be found all the latest information which is available.

Finally, the writer is much indebted and wishes to express his thanks to all those, from the East as well as from the West, whom it has been a pleasant duty to meet during the year, and without whose willing aid it would not have been possible to compile this review.

[70] *Nature*, Dec. 8, 1921, 457.
[71] H.M. Stationery Office, 1921.

FINE CHEMICALS, MEDICINAL SUBSTANCES AND ESSENTIAL OILS.

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Alkaloids.

Cinchona Alkaloids.

Of all the alkaloids, the cinchona group continues to attract the greatest amount of attention. The Dutch, by reason of the foresight shown in developing the cinchona plantations in Java over a number of years, still have a monopoly of cinchona bark. Japan, America, and the British Empire are, however, exhibiting a growing interest in cinchona cultivation, and an important scheme has been initiated for developing the production of quinine in India.[1] As a result Burma will, in time, probably become an important source of cinchona both for India, which already produces a not inconsiderable quantity of quinine, and for the British Empire.[2] The necessity for the scientific cultivation of cinchona in our own colonies has been emphasised by Sir William Pope in his presidential address to the Society.[3] In the Cameroons and East Africa, former German colonies, the experimental plantations have furnished a bark of good quality.[4] The Japanese have the matter well in hand and have secured 800,000 acres of land on the slopes of the Andes, the natural habitat of cinchona, and are growing cinchona and coca.[5]

H. W. Acton and his collaborators have recently published the detailed evidence on the use of quinine and cinchona febrifuge in the treatment of benign tertian and in malignant malaria.[6] In benign tertian, the febrifuge is better than quinine, and its use, if adopted in India, would involve a saving of 46%; it could, moreover, be supplied from her own plantations. This work led

[1] *Calcutta Gazette*, Dec. 8th, 1920.
[2] *J.*, 1921, 126R.
[3] *J.*, 1921, 180T.
[4] *J.*, 1921, 382R.
[5] *J.*, 1921, 413R.
[6] *Ind. J. Med. Res.*, 1921, **8**, 737-871.

to the later developments in which the component alkaloids of the febrifuge were tried individually. The results obtained were described in the previous report.[7]

The use of quinidine for the restoration of normal cardiac rhythm in cases of auricular fibrillation has attracted considerable attention in recent years. Originally discovered by Wenckebach, this recovery of normal rhythm lasting from a few days to several months, has been observed in 50% of the cases in the hands of several workers.[8]

During the past year a great advance has been made from several sides towards the synthesis of the sixteen possible stereoisomerides of hydrocinchonine, of which only one other, hydrocinchonidine, was known previously. The reduction of hydrocinchoninone, $C_9H_6N{\cdot}CO{\cdot}C_9H_{16}N$, by zinc dust or powdered aluminium in the presence of alcohol and sodium ethoxide has given rise to the four possible stereoisomeric alcohols, two of which are hydrocinchonine and hydrocinchonidine, whilst the remaining two are new.[9] 3-Ethyl-4-methylpyridine, the starting point for the synthesis of the hydro-alkaloids, has been synthesised in two ways,[10] and has been converted into homocincholeupone.[11]

$$NH\begin{cases} CH_2\cdot CH_2 \\ CH_2\cdot CHEt \end{cases}\!\!\!\!\!\!> CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

This should occur in two racemic forms, only one of which has been obtained, and this, so far, has resisted resolution. One of its optically active forms is, however, a degradation product of hydrocinchonine and has been condensed in the form of the ethyl ester of its N-benzoyl derivative with quinoline-4-carboxylic acid ethyl ester, yielding an ester which, on hydrolysis, gave hydrocinchotoxine,[12] which can be converted by well-known methods into hydrocinchoninone. The progress in the quinine, hydroquinine, and cinchonine series is not so marked, the difficulties to be surmounted being greater.

[7] *Ann. Repts.*, 1920, **5**, 487.

[8] A. N. Drury and C. C. Iliescu, *Brit. Med. J.*, 1921, **2**, 511; T. Lewis, A. N. Drury, C. C. Iliescu, and A. M. Wedd. *ibid.*, 514. W. Frey, *Berl. Klin. Wochsch.*, 1918, 417, 849. R. L. Levy, *J. Amer. Med. Assoc.*, 1921, **76**, 1289. A. W. M. Ellis and A. E. Clark-Kennedy, *Lancet*, 1921, **2**, 894. E. Jenny, *Schweiz. Med. Wochsch.*, 1921, **51**, 272. F. C. Arrilaga and C. P. Waldorp, *Physiol. Abst.*, 1921, **6**, 389.

[9] Vereinigte Chininfabr. Zimmer u. Co., G.P. 330,813; *J.*, 1921, 449A.

[10] P. Rabe and E. Jantzen, *Ber.*, 1921, **54**, 925; *J. Chem. Soc.*, 1921, i., 438. L. Ruzicka and V. Fornasir, *ibid.*, 1920, i., 550.

[11] E. Koenigs and W. Ottmann, *Ber.*, 1921, **54**, 1343; *J. Chem. Soc.*, 1921, i., 595.

[12] Vereinigte Chininfabr. Zimmer u. Co., G.P. 330,945; *J.*, 1921, 449A.

Several workers[13] have synthesised quinine-like compounds, and the latest contribution to this subject is by L. Ruzicka,[14] who has condensed the esters of quinolinecarboxylic acids with methyl-2-piperidone and allied compounds to yield substances which are hydrolysed to aliphatic quinotoxines :—

$$C_9H_6N{\cdot}CO_2Et + CH_2\left\langle\begin{matrix}CH_2\cdot CH_2\\ CO\ \cdot NMe\end{matrix}\right\rangle CH_2 \rightarrow$$

$$C_9H_6N{\cdot}CO{\cdot}CH\left\langle\begin{matrix}CH_2{\cdot}CH_2\\ CO{\cdot}NMe\end{matrix}\right\rangle CH_2 \rightarrow C_9H_6N.CO{\cdot}(CH_2)_4{\cdot}NHMe.$$

These, on treatment with bromine and removal of hydrogen bromide, yield with ring-formation, quinolylpyrrolidyl ketones :—

$$C_9H_6N{\cdot}CO{\cdot}(CH_2)_4{\cdot}NBrMe \rightarrow C_9H_6N{\cdot}CO{\cdot}CH\left\langle\begin{matrix}CH_2{\cdot}CH_2\\ | \\ NMe{\cdot}CH_2\end{matrix}\right.$$

The substitution derivatives of cinchona alkaloids continue to be attacked from various quarters. Whilst W. A. Jacobs and M. Heidelberger,[15] continuing their investigations in this series, have coupled the 5-amino-derivatives of the hydro-alkaloids with diazotised aromatic amines, G. Giemsa and J. Halberkann have diazotised the 5-amino-derivatives with formation of diazo-anhydrides, which on boiling in acid or alkaline solution, yield a new type of compound of unknown constitution.[16] Patents have been taken out for the preparation of the amino-compounds of cinchona alkaloids, for the nitro- and amino-sulphonic acids of the hydro-alkaloids, and for the corresponding nitrohydro-alkaloids produced by hydrolysis.[17] The production of cinchona alkaloids containing selenium and said to be of therapeutic value is also the subject-matter of a patent.[18]

Hyoscine.

The alkaloid hyoscine finds a number of applications in medicine, but our knowledge of the pharmacological properties of the optical isomerides has hitherto been imperfect. A. R. Cushny,[19] working with the pure *d*- and *l*-hyoscines prepared by the writer,[20] now

[13] A. Kaufmann, *J.*, 1913, 709. P. Rabe, R. Pasternack, and K. Kindler, *J. Chem. Soc.*, 1917, i., 283. P. Karrer, *ibid.*, 1918, i., 38. *Cf. also Ann. Repts.*, 1917, **2**, 487.

[14] *Ber.*, 1921, **54**, 1189 ; *J. Chem. Soc.*, 1921, i., 585.

[15] *J. Amer. Chem. Soc.*, 1920, **42**, 2278 ; *J.*, 1921, 96A.

[16] *Ber.*, 1921, **54**, 1167 ; *J. Chem. Soc.*, 1921, i., 581.

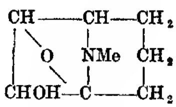
[17] C. F. Boehringer, G.P. 335,113 ; *J.*, 1921, 489A ; G.P. 338,738, *J.*, 1921, 749A ; G.P. 339,947, *J.*, 1921, 828A.

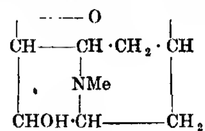
[18] Vereinigte Chininfabr. Zimmer u. Co., G.P. 331,145 ; *J.*, 1921, 280A.

[19] *J. Pharm. Exp. Ther.*, 1921, **17**, 41.

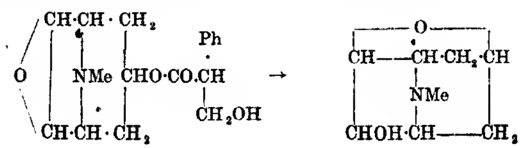
[20] H. King, *Chem. Soc. Trans.*, 1919, **115**, 476, 974.

finds that *l*-hyoscine is 15 to 18 times as powerful as *d*-hyoscine in its action on the nerve terminations in the salivary glands and in other "specific" atropine effects, but that on the nerve endings in striated muscle, on unstriated muscle and on the central nervous system, their action is identical. The use of hyoscine in "twilight sleep," and as a sedative in mania is thus independent of the optical purity of the substance, but as a mydriatic, the optimum effect is obtained by using the pure *lævo*-form. The constitution of the basic portion of the molecule of hyoscine, namely oscine (or scopoline), still remains uncertain in respect of the position of the oxygen bridge. K. Hess,[21] from a study of the exhaustive methylation of oscine, which proceeds anomalously, concluded that the bridge was as in I., whilst Gadamer and F. Hammer,[22] utilising the optically active oscines for the Hofmann degradation, adopt


I.


II.

the formula II., put forward by the writer. Hess has now effected the Hofmann degradation in a more normal manner[23] and adheres to his formulation. In hyoscine Gadamer and Hammer consider that the oscine residue has a symmetrical configuration and that an unsymmetrical oscine is formed on hydrolysis, a possibility which was also pointed out by the present writer.



Ergot.

A resuscitation of this question is unexpected. A Swiss firm in 1919 covered by patent a process for the isolation of a highly active preparation of ergot.[24] Powdered ergot is treated with a weak acid or with acid salts, *e.g.*, aluminium, ferrous, or copper sulphates, to fix the basic constituents, and then extracted with an organic solvent to remove fats and phytosterols. The tissue is mixed with

[21] *Arch. Pharm.*, 1921, **259**, 110; *J. Chem. Soc.* 1920, i., 81.
[22] *Arch. Pharm.*, 1921, **259**, 110; *ibid.*, 1921, i., 588.
[23] *Z. angew. Chem.*, 1921, **34**, 393; *ibid.*, 1921, i., 683.
[24] Chem. Fabr. vorm. Sandoz, E.P. 125,396; *J.*, 1920, 349A.

more solvent and the acid neutralised by baryta. The alkaloids are then extracted. The crude alkaloid is purified from acetone containing 5–10% of water.[25] Similar processes have been applied to other alkaloids, *e.g.*, hyoscyamine, morphine, pilocarpine,[26] etc. The properties of the pure alkaloid of ergot so isolated have been described by K. Spiro and A. Stoll.[27] It is called ergotamine, has the formula $C_{33}H_{35}N_5O_5$, is crystalline, forms crystalline salts, and has the full physiological activity of ergot. It is converted into an isomeride, ergotaminine, by warming with methyl alcohol. The authors have not apparently had in hand for comparison the amorphous ergotoxine, $C_{35}H_{41}O_6N_5$, of Barger and Carr and of Tanret, which forms crystalline salts, has the pharmacological activity of ergot, and treated with methyl alcohol gives crystalline ergotinine, $C_{35}H_{39}O_5N_5$. The parallelism in the properties of the alkaloids of the two groups of workers is much closer than is here indicated. It is therefore unfortunate that new claims and new nomenclature should be advanced without the real justification supplied by a direct comparison. It is, however, possible that different varieties of ergot contain different but related alkaloids. The chemistry of the ergot alkaloids is admittedly in an unsatisfactory state owing to the rarity of the substances and to that extent the work of Spiro and Stoll, of which this is a preliminary publication, will be looked forward to with interest.

Other Alkaloids.

The patents taken out by R. Willstätter for the preparation of tropinonecarboxylic acid esters, tropinone, and ecgonine were referred to in last year's report.[28] A full description of the processes has now appeared,[29] the important end-products being tropinone and ψ-ecgonine, which latter on esterification and benzoylation gives ψ-cocaine. The starting point of this important synthetic method is acetonedicarboxylic acid, which by electrolysis of the di-potassium derivative of its mono-ethyl ester gives ethyl succinyldiacetate.[30]

$$CO_2Et.CH_2.C(OK):CH.CO_2K \rightarrow C_2H_4(CO.CH_2.CO_2Et)_2$$

A contribution to the chemistry of physostigmine of considerable potential value has been made by E. Stedman.[31] Physostigmine

[25] E.P. 140,056; *J.*, 1921, 128A.

[26] E.P. 131,283; *J.*, 1920, 436A. E.P. 134,197; *J.*, 1920, 675A. E.P. 153,219; *J.*, 1920, 833A.

[27] *Schweiz. Med. Wochsch.*, 1921, No. 23.

[28] *Ann. Repts.*, 1920, **5**, 499.

[29] R. Willstätter and M. Bommer, *Annalen*, 1921, **422**, 15; *J.*, 1921, 127A.

[30] R. Willstätter and A. Pfannenstiel, *Annalen*, 1921, **422**, 1; *J. Chem. Soc.*, 1921, i., 91.

[31] *Chem. Soc. Trans.*, 1921, **119**, 891.

or eserine, $C_{15}H_{21}O_2N_3$, on hydrolysis loses carbon dioxide and methylamine, yielding eseroline, $C_{13}H_{18}ON_2$, the methiodide of which on heating with sodium ethoxide and methyl iodide has now been converted into a compound $C_{10}H_{17}ON_2I$, which contains three alkyl-groups, the nuclear arrangement thus containing seven carbon atoms. This should lead to the elucidation of the constitution of this useful alkaloid and so eventually to synthetic experiments on similarly constituted bases.

Lobelia inflata, or Indian tobacco, is a North American plant which has found application in the treatment of asthma. A process for obtaining its little known ingredients is the subject of a patent.[32] The plant contains three alkaloids, of which α-lobeline is crystalline, possesses the characteristic pharmacological action of *Lobelia inflata*, and is now available as a commercial product. The alkaloids have recently been examined chemically by H. Wieland, who ascribes the formula, $C_{23}H_{29}O_2N$, to α-lobeline and finds acetophenone as a product of hydrolysis.[33]

Simple Natural Bases.

Choline is a common constituent of plant and animal tissues and a few of its esters have been found to occur naturally. A. J. Ewins[34] isolated acetylcholine from a sample of ergot in 1914 and the same substance has now been found in Shepherd's purse (*Capsella bursa-pastoris* L.),[35] an extract of which was employed during the war as a substitute for ergot. The possibility that the esters with the naturally occurring amino-acids may be of pharmacological importance is being examined by H. W. Dudley, who has prepared glycylcholine, $NMe_3Cl.C_2H_4O.CO.CH_2NH_2$, but its physiological behaviour is not recorded.[36] A group of related substances has been prepared by P. Karrer and co-workers,[37] who reduce the esters of the naturally occurring amino-acids or their acetyl-derivatives to the corresponding alcohol by means of sodium and alcohol, and then completely methylate the amino-group :—

$$NH_2.CHR.CO_2Et \rightarrow NH_2.CHR.CH_2OH \rightarrow NMe_3I.CHR.CH_2OH$$

The yields are very poor, so that other synthetic processes are also employed. Leucinecholine has a weak action on the uterus, but its effect is increased by acetylation. Phenylalaninecholine, on the other hand, is reported to be very potent.

32 C. H. Boehringer Sohn, E.P. 145,621 and 145,622 ; *J.*, 1921, 195A, 448A.

33 *Ber.*, 1921, **54**, 1784 ; *J.*, 1921, 788A.

34 *J.*, 1914, 664.

35 H. Boruttau and H. Cappenberg, *Arch. Pharm.*, 1921, **259**, 33 ; *J.*, 1921, 276A. C. Grimme, *Pharm. Zentralh.*, 1921, **62**, 495 ; *J.*, 1921, 748A. H. Cappenberg, *Pharm. Zentralh.*, 1921, **62**, 560 ; *J.*, 1921, 748A. *Cf. also* H. H. van Urk, *Pharm. Weekblad*, 1921, **58**, 553 ; *J.*, 1921, 409A.

36 *Chem. Soc. Trans.*, 1921, **119**, 1256 ; *J.*, 1921, 714A.

37 *Helv. Chim. Acta*, 1921, **4**, 76 ; *J. Chem. Soc.*, 1921, i., 228.

The isolation and identification of the pituitary active principles is proving a very difficult problem. H. W. Dudley in 1919 advanced experimental evidence which seemed to show that the specific pressor and oxytocic principles are different substances.[38] Further evidence which points in the same direction is now adduced by H. H. Dale and H. W. Dudley.[39] These authors show also, in agreement with Abel and Nagayama's findings,[40] that the active principles are destroyed by boiling with 0·5% hydrochloric acid; they cannot, however, adduce any evidence that there is a relation between histamine and the specific action of the extract. J. Roca[41] has examined the relative amounts of depressor and broncho-constrictor substances obtainable from the anterior and posterior lobes of the fresh pituitary gland after destruction of the specific pressor principle, and finds 7 to 8 times as much depressor substance in the posterior as in the anterior lobe. From its general behaviour he thinks it may be histamine.

Histamine has been isolated from the products of putrefaction of polished rice[42] and has been found in a hot water extract of the egg-plant (*Solanum melongena* L.).[43] *exo*-N-Methylhistamine has been prepared by F. L. Pyman and R. G. Fargher by decarboxylation of *exo*-N-methylhistidine.[44] Its actions on the blood pressure and on the uterus are respectively about one two-hundredth and one eightieth those of histamine.[45] By condensing histamine with methylal, S. Fränkel and K. Zeimer obtained tetrahydropyrido-3.4-iminazole,

$$CH\begin{array}{l}\diagup NH\cdot C\cdot CH_2\cdot CH_2 \\ \qquad\quad \| \qquad\qquad | \\ \diagdown N\cdot C\cdot CH_2\cdot NH\end{array}$$

which was stated to be superior in activity to histamine. A re-examination of this substance by Dale and Dudley shows that in reality it has only one fifteen-hundredth the activity of histamine on uterine muscle and no significant action on the blood-pressure.[45]

A. Windaus and O. Dalmer have prepared β-2-furylethylamine and its tetrahydro-derivative with a view to finding an outlet for derivatives of furfuraldehyde.[46] The oxytocic activity is, however, small, being one quarter and one half, respectively, that of hydr-

[38] *J. Pharm. Exp. Ther.*, 1919, **14**, 295.

[39] *Ibid.*, 1921, **18**, 27.

[40] *Ibid.*, 1920, **15**, 347.

[41] *Ibid.*, 1921, **18**, 1.

[42] K. Yoshimura and K. Chenfon, *J. Chem. Soc., Japan*, 1921, **42**, 22; *J.*, 1921, 275A.

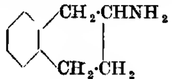
[43] K. Yoshimura, *J. Chem. Soc., Japan*, 1921, **42**, 16; *J. Chem. Soc.*, 1921, i., 296.

[44] *Chem. Soc. Trans.*, 1921, **119**, 734; *J.*, 1921, 487A.

[45] H. H. Dale and H. W. Dudley, *J. Pharm. Exp. Ther.*, 1921, **18**, 103.

[46] *Ber.*, 1920, **53**, 2304; *J. Chem. Soc.*, 1921, i., 117.

astinine. Piperonalcyanhydrin, $CH_2O_2 : C_6H_3.CHOH.CN$, has been reduced to the corresponding hydroxyethylamine derivative, $CH_2O_2 : C_6H_3.CHOH.CH_2.NH_2$ which bears some relation to adrenaline. Its physiological action has not been recorded but would probably be negligible.[47] The sympathomimetic action of *ac*-β-tetrahydronaphthylamine (I.) was demonstrated by Dale and G. Barger and by Jonescu.[48] By the introduction of a hydroxyl-group in the *α*-position and various alkyl groups into the amino-group, a number of derivatives of the hydroxyamine (II.) have been patented and are stated to be very active physiologically[49] :—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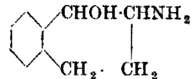

II.

What appear to be the preliminary stages of the synthesis of thyroxin have been published by E. C. Kendall and A. E. Osterberg, who record the synthesis of cyclohexane derivatives on a fairly large scale.[50] The published evidence for the now familiar formula ascribed to thyroxin by these authors would hardly seem sufficient to justify syntheses in the cyclohexane series. The question as to whether the iodine or the nuclear arrangement is responsible for the specific action of thyroxin is receiving attention from these authors in synthetic experiments, but the detailed evidence is not yet available.[51]

Glucosides and Neutral Principles.

A contribution to the chemistry of digitalis has been made by M. Cloetta.[52] The position of the subject previous to this was substantially that described in a previous report.[53] The claim is now made that digitoxin has been obtained pure and of constant m.p. 252° C., when crystallised from a mixture of chloroform and ether. It has the formula $C_{44}H_{70}O_{14}$, and on hydrolysis with hydrochloric acid in aqueous alcohol at room temperature gives rise to digitoxigenin, m.p. 245° C., two molecules of digitoxose, m.p. 107° C., and a third substance which is an oil and probably has the formula $C_8H_{14}O_4$. This latter substance probably corresponds to the resin which is obtained together with digitoxose by hydrolysis by Kiliani's method using hot hydrochloric acid (0·5%). When heated in a very high vacuum above the temperature of its melting point digitoxin yields a volatile crystalline compound

[47] F. A. Mason, *Chem. Soc. Trans.*, 1921, **119**, 1077.
[48] *J. Physiol.*, 1910, **12**, 19.
[49] Tetralin G.m.b.H., G.P. 335,476 ; *J.*, 1921, 503A.
[50] *J. Amer. Chem. Soc.*, 1920, **42**, 2616 ; *J. Chem. Soc.*, 1921, i., 101.
[51] E. C. Kendall, *Surg. Gynec. Obstet.*, 1921, **32**, 205.
[52] *Arch. Exp. Path. Pharm.*, 1920, **88**, 113 ; *J. Chem. Soc.*, 1921, i., 39.
[53] *Ann. Repts.*, 1918, 3, 290.

$C_8H_{14}O_4$, m.p. 116° C. The non-volatile residue, called digitan, has the formula $C_{36}H_{56}O_{10}$, and on hydrolysis gives two molecules of digitoxose and one of digitoxigenin.

$$\underset{\text{Digitan.}}{C_{36}H_{56}O_{10}} + 2H_2O = \underset{\text{Digitoxigenin.}}{C_{24}H_{36}O_4} + \underset{\text{Digitoxose.}}{2C_6H_{12}O_4}$$

The volatile crystalline substance corresponds therefore to the oily substance obtained on hydrolysis of digitoxin.

Digitoxin and digitan have the same powerful action on the frog's heart and an action of the same character on mammals. Digitoxigenin, which is no longer glucosidic, still possesses a marked action on the frog's heart but in addition it acts as a convulsive poison. It is possible that this latter action is responsible for certain undesirable secondary effects observed in man in digitalis therapy. The digitoxins of Kiliani are considered by Cloetta to be mixtures of varying degrees of purity, whilst his digitophyllin is probably almost pure digitoxin, as its analytical figures, crystalline form, solubility, and hydrolysis agree with the pure digitoxin now obtained. The digitoxins and digitalins of commerce, though crystalline, are mixtures from which pure digitoxin with m.p. 252° C. can be isolated.

A new reagent which may prove useful for the synthesis of α-glucosides and disaccharides of the α-series is described by A. Pictet and P. Castan.[54] α-Glucosan, the anhydride of glucose, is converted by concentrated hydrochloric acid into α-glucosyl chloride, $C_6H_{11}O_5Cl$, which has a reactive chlorine atom attached to the first carbon atom of the chain. By the action of sodium methoxide it is converted into α-methylglucoside and by potassium glucosan into α-glucosidoglucose, a crystalline sugar resembling gentiobiose.

Glycyrrhizin, the sweet principle of liquorice root, has been submitted to further examination.[55] It was originally described as containing nitrogen, but this is shown to be incorrect. On hydrolysis it yields glycyrrhetic acid and two molecules of glycuronic acid lactone. The reaction is, however, a complex one.

Hyenanche globosa, a South African plant, said to have been used for poisoning hyenas, has been shown by T. A. Henry[56] to contain hyenanchin, a convulsant, non-nitrogenous poison, $C_{15}H_{18}O_7$. It is crystalline and its reactions show that it probably belongs to the group of similar poisons represented by picrotoxinin, coryamirtin, and tutin. It is accompanied in the plant by an isomeride, *iso*-hyenanchin, which is relatively non-toxic. Both substances are lactones.

[54] *Helv. Chim. Acta*, 1921, **4**, 319; *J. Chem. Soc.*, 1921, i., 396.

[55] P. Karrer, W. Karrer, and J. C. Chao, *Helv. Chim. Acta*, 1921, **4**, 100; *J.*, 1921, 194A.

[56] *Chem. Soc. Trans.*, 1920, **117**, 1619; *J.*, 1921, 97A.

Some years ago J. J. Abel and D. I. Macht[57] isolated a neutral principle bufagin, $C_{18}H_{24}O_4$, from the parotid gland of the tropical toad. Its action physiologically was that of the digitalis group. The same substance was found later in "senso," a Chinese drug prepared from toad-skins, together with bufotoxin, a member of the picrotoxin group of poisons, but this latter substance was not obtained pure.[58] Bufotoxin has now been prepared crystalline from the same source and has the formula $C_8H_{10}O_2$.[59] Bufotalin, $C_{16}H_{24}O_4$, the poisonous principle of the common toad, resembles bufagin but is not identical with it. Like other members of this group of neutral principles it is a lactone.[60]

Essential Oils.

In the production of camphor, Japan still controls the major supply, the record production for 1916 being 8·4 million lb.[61] The acreage of artificially planted camphor trees is, however, being rapidly extended in various parts of the world, there being over 15,000 acres in the United States alone, with an eventual yield of 120 to 150 lb. of camphor per acre.[62] The first camphor farm in Florida has placed 10,000 lb. of camphor on the market since the beginning of the year.[63] The maximum yield of camphor not being obtained till the trees are 50 to 60 years old, necessitates the use of leaves and twigs of younger trees with the disadvantage of smaller camphor content and absence of valuable by-products of the camphor-oil, *e.g.*, safrole,[64] which, in addition to other uses, serves as a basis for the preparation of piperonal.[65] The production of isoprene from light camphor oils in small yield has been shown to occur by passing the oil over various catalysts at 500° C.[66]

The synthetic production of camphor continues to attract the attention of celluloid manufacturers. Economically the problem is an extremely difficult one, and is primarily dependent on a plentiful supply of turpentine rich in pinene. This limits the countries for its successful production to a few. During the war,

[57] *J. Chem. Soc.*, 1912, ii., 1194.

[58] S. Shimizu, *J. Chem. Soc.*, 1916, i., 698. *Cf.* G. Barger, *J.*, 1918, 33T.

[59] K. Kodama, *Physiol. Abs.*, 1921, 487.

[60] H. Wieland and F. J. Weil, *J. Chem. Soc.*, 1913, i., 1343. C. H. Boehringer, G.P. 248,737 and 282,751. *Cf.* H. Handovsky, *J. Chem. Soc.*, 1920, i., 495.

[61] *J.*, 1921, 148R.

[62] *J.*, 1921, 237R, 379R.

[63] *J.*, 1921, 388R.

[64] *J.*, 1921, 254R.

[65] S. Nagai, *J. Chem. Soc.*, 1920, i., [illegible]

[66] Y. Nishizawa, *J. Tokyo Chem. Soc.*, 1920, 41, 1048; *J. Chem. Soc.*, 1921, i., 217.

owing to the failure of outside supplies, the Schering interests in Germany manufactured synthetic camphor; in the United States the present trade depression has caused the suspension of work on the erection of a synthetic camphor plant to work a German process.[67] A. Dubosc and A. Luttringer have described various methods for the preparation of bornyl esters, chiefly the formate (a possible intermediate product in the preparation of camphor), by the action of formic acid on pinene hydrochloride in the presence of various reagents, *e.g.*, sodium formate, zinc powder, iron filings; and processes for oxidising the bornyl esters to camphor by means of peroxides are described.[68] The production of borneol from turpentine or crude pinene by the action of tetrachlorophthalic acid is the subject-matter of two patents.[69] Unlike the product of the action of other acids on pinene, the borneol is free from *iso*-borneol and is optically active. This might be of importance where a pharmaceutically pure camphor is required, although pharmacologically there is little or no difference between the action of *d*-, *l*-, and *r*-camphors.[70] When heated with a carboxylic acid, pinene hydrochloride in presence of 5% or less of zinc gives the *iso*-bornyl ester and camphene.[71]

The production of synthetic substitutes for camphor is a phase of the question which has not been lost sight of, and a valuable account of the progress to date has been given by A. P. Sachs and O. Byron.[72] Various diaryldialkylcarbamides have recently been protected. They are miscible in all proportions with organic solvents and with collodion.[73]

The universal prevalence[74] of hookworm infections among the natives of tropical countries is a source of great economic loss. The campaigns[75] against this disease show that the most valuable anthelminthics are chenopodium oil, followed closely by thymol and β-naphthol.[76] J. F. Caius and K. S. Mhaskar, having a good supply of clinical material, have correlated the action of anthelmin-

[67] *J.*, 1921, 388R.

[68] *Bull. Soc. Ind. Rouen*, 1920, **48**, 88, 89; *J. Chem. Soc.*, 1921, i., 115, 116.

[69] Fabr. de Prod. Chim. de Thann et de Mulhouse, E.P. 144,604 and 158,533; *J.*, 1921, 369A, 561A.

[70] G. Joachimoglu, *Arch. Exp. Path. Pharm.*, 1920, **88**, 364; *J. Chem. Soc.*, 1921, i., 146.

[71] L. G. Wesson, U.S.P. 1,372,382; *J.*, 1921, 369A.

[72] *J. Ind. Eng. Chem.*, 1921. **13**, 893.

[73] Fabr. de Prod. Chim. Organique de Laire, G.P. 323,534; *J. Chem. Soc.*, 1920, i., 879. *Cf.* H. E. Herz, *J.*, 1921, 365R.

[74] K. S. Mhaskar, *Ind. J. Med. Res.*, 1919-20, **7**, 428. J. W. D. Megaw, *ibid.*, 840.

[75] *Ann. Repts.*, 1919, 4, 497. *Trop. Dis. Bull.*, 1921, **18**, 124. *Proc. Roy. Soc. Med.*, 1921, **14**, 72.

[76] J. F. Caius and K. S. Mhaskar, *Ind. J. Med. Res.*, 1921, **9**, 33.

thics with their chemical composition.[77] Oil of chenopodium was found best, being a powerful vermicide; it suffers however from the disadvantage that there is no simple and accurate method of determining the optimum dose, owing to variations in the ascaridole content. The constituents of *oleum chenopodii* have been re-examined by T. A. Henry and H. Paget, who definitely prove that the active principle is ascaridole, the remaining hydrocarbon fraction being inactive.[78] The same oil acts as an efficient vermifuge for strongyloides infections[79] and other intestinal parasites.[80] A number of other essential oils were examined by Caius and Mhaskar, but only *oleum eucalypti* had any anthelminthic action and this slight. Thymol, the dosage of which is certain, had powerful vermicidal and mild vermifugal properties.

Baker and Smith's classic "Research on the Eucalypts and their Essential Oils" has reached a second edition.[81] These unique oils of the southern hemisphere are attracting an ever-increasing circle of investigators. Two constituents, phellandrene and piperitone, are now commercial products.[82] The constitution of the latter substance, about which there was some doubt, has now been elucidated. Piperitone as it occurs naturally in various species of eucalyptus is lævorotatory, but is racemised by alkali or heat.[83] The dextro-form occurs to the extent of 45% in the essential oil of *Cymbopogon sennarensis*,[84] in oil of Japanese peppermint,[85] in camphor oil, and in the oil from *Andropogon iwaranacusa*[86] to the extent of over 70%. The products of oxidation, especially diosphenol,[87, 88] prove it to be Δ^1-*p*-menthene-3-one. On oxidation with ferric chloride and acetic acid, piperitone gives a 25% yield of thymol.[89] A cheapening of this process and a better yield would probably enable thymol from this source to be a commercial proposition.

Cymene, the chief constituent of spruce turpentine, to which reference has been made in a previous report,[90] still serves as a

77 *Ind. J. Med. Res.*, 1919-20, **7**, 429, 570, 602, 606, 722; *ibid.*, 1920-21, **8**, 125, 373, 379, 384, 737.

78 *Chem. Soc. Trans.*, 1921, **119**, 1714; *J.*, 1922, 33A.

79 H. H. Willis, *Trop. Dis. Bull.*, 1921, **18**, 116.

80 E. R. Royer, *J. Amer. Med. Assoc.*, 1920, **75**, 1702.

81 *J.*, 1921, 183R.

82 *Perf. Essent. Oil Rec.*, 1920, **11**, 361.

83 J. Reed and H. G. Smith, *Chem. Soc. Trans.*, 1921, **119**, 779; *J.*, 1921, 560A.

84 O. D. Roberts, *J.*, 1915, 1165.

85 Schimmel's Rep., 1910, Oct., 1897.

86 J. L. Simonsen, *Chem. Soc. Trans.*, 1921, **119**, 1644; *J.*, 1921, 869A.

87 A. R. Penfold, *Proc. Roy. Soc.*, *N.S.W.*, Aug. 3rd, 1921.

88 *Perf. Essent. Oil Rec.*, 1921, **12**, 21.

89 *Ibid.*, 21.

90 *Ann. Repts.*, 1919, **4**, 496; 1920, **5**, 496.

subject of much investigation. Its oxidation by air under pressure has been examined,[91] and its conversion into *p*-nitrotoluene-*o*-sulphonic acid, which can serve as the basis of stilbene colouring matters.[92] Its purification and use as a solvent have been described by A. S. Wheeler,[93] whilst the electrolytic reduction of nitrocymene and conversion into thymol,[94] and its conversion into nitroamino-derivatives; diamino-derivatives, benzidine-derivatives, and sulphonic acids are the subject-matter of patents.[95]

Comparatively little is known about the odorous principles of fruits. Kleber about a decade ago showed that banana contained amyl acetate.[96] F. B. Power and V. K. Chesnut, as a result of their examination of ripe apples,[97] have covered by patent,[98] a synthetic apple oil consisting of the amyl esters of formic, acetic, caproic, and caprylic acids, together with acetaldehyde. The same authors have examined the odorous constituents of peaches and find present the formic, acetic, valeric, capric, and caprylic esters of linalool, together with some acetaldehyde.[99] The possibility of utilising the hydrolytic products of proteins (a process carried out on the manufacturing scale in Japan) for the production of nitrogen-free esters with a fragrant odour has been examined by S. Kodama, who prepared several substituted esters from *iso*-hexoic acid.[100]

Great activity is being shown by the Japanese in the examination of the essential oils of eastern plants. The majority of the constituents when characterised are identical with the constituents of better-known oils. Of special interest is perillic aldehyde, $C_{10}H_{14}O$, isolated to the extent of 44–57% from *Perilla nankinensis*.[101] Its *a*-antioxime is stated to be 2000 times as sweet as cane sugar. The corresponding nitrile is one half as sweet as saccharin, whilst the *β*-synoxime lacks sweetness. F. W. Semmler and B. Zaar, who first isolated this aldehyde, attributed to it the constitution 4-*iso*-propenyltetrahydrobenzaldehyde.[102]

The estimation of cineole in eucalyptus oil[103] forms the subject of

[91] H. Schrader, *Ges. Abhandl. Kennt. Kohle*, 4, 310; *J. Chem. Soc.*, 1921, i., 329.

[92] S. V. Hintikka, *Ann. Acad. Soc. Fennicæ*, 1917, **10**, 1; *J. Chem. Soc.*, 1921, i., 332.

[93] *J. Amer. Chem. Soc.*, 1920, **42**, 1842.

[94] R. M. Cole, U.S.P. 1,378,939; *J.*, 1921. 561A.

[95] The Selden Co., U.S.P. 1,314,923, 1,314,924 and 1,314,927; *J.*, 1921, 323A.

[96] *J.*, 1913, 104.

[97] *J.*, 1920, 609A.

[98] U.S.P. 1,366,541; *J.*, 1921, 195A.

[99] *J. Amer. Chem. Soc.*, 1921, **43**, 1775.

[100] *J. Tokyo Chem. Soc.*, 1920, **41**, 965; *J. Chem. Soc.*, 1921, i., 220.

[101] S. Furukawa and Z. Tomizawa, *J. Chem. Soc.*, 1920, i., 750.

[102] *J.*, 1911, 154.

[103] *Ann. Repts.*, 1916, **1**, 297.

several communications. An improvement on all previous methods has been effected by the introduction by T. T. Cocking of the use of the addition compound with *o*-cresol.[104] Its application was limited to oils containing 45% or more of cineole, but the same author has now shown how it can be applied to oils of lower cineole content.[105]

Synthetic Drugs.

Organo-Metallic Compounds.

A glance through the publications in organic chemistry of the last few years shows that a fair percentage of the labours of organic chemists is devoted to developments in the organo-metallic compounds. The past year is no exception. The incentive has been largely due to the action of these substances on living tissues or protoplasm, whether the products be designed for chemical warfare on man or his parasites.

Arsenic Compounds.—The search for the cause of the variation of toxicity shown by commercial samples of salvarsan has given rise to an immense volume of work. The concensus of opinion, now, is that it is physical,[106] being intimately bound up with the colloidal properties of the substance. A valuable analysis of the physical factors concerned has been given by C. N. Myers.[107] The physical state is, however, influenced by the presence of foreign substances. The constituent of salvarsan containing sulphur, insoluble in methyl alcohol and isolated by Fargher and Pyman,[108] has now been shown by the writer to consist of the monosulphonic acid of salvarsan associated with varying proportions of salvarsan sulphate.[109] The chemotherapeutic index, I, which is the ratio of the curative dose, C, to the maximum tolerated dose, T, as determined on mice infected with *Trypanosoma equiperdum*, for the sulphonic acid is 1·4·5, whereas pure salvarsan, free from sulphur, prepared by the use of hypophosphorous acid, has an index of 1·13·5. The presence of this monosulphonic acid in salvarsan, from the point of view of its contribution to the therapeutic efficiency, is therefore undesirable. Pure salvarsan prepared by reduction of 3-amino-4-hydroxyphenyl-arsinic acid by hypophosphorous acid has the disadvantage of low solubility.[108, 110] By first reducing the acid to the oxide by means of hydriodic acid and sulphur dioxide and continuing the reduction

[104] *J.*, 1920, 610A; 1921, 162A, 238A.

[105] *Perf. Essent. Oil Rec.*, 1921, **12**, 339; *J.*, 1921, 869A.

[106] *M.R.C. Rep.*, No. 44, Reid Hunt, *J. Amer. Med. Assoc.*, 1921, **76**, 854.

[107] *J. Laborat. Clin. Med.*, 1921, **7**, 17.

[108] *J.*, 1920, 465A; *Ann. Repts.*, 1920, **5**, 501.

[109] H. King, *Chem. Soc. Trans.*, 1921, **119**, 1107, 1415; *J.*, 1921, 636A, 789A.

[110] W. G. Christiansen, *J. Amer. Chem. Soc.*, 1920, **42**, 2402; *J.*, 1921, 97A; *Ann. Repts.*, 1920, **5**, 501.

to the arseno-stage by hypophosphorous acid, it is now shown that the product is more soluble.[111] A number of compounds which might possibly occur in commercial salvarsan through the use of impure materials have been prepared and examined therapeutically by G. W. Raiziss and J. L. Gavron.[112]

E. Fourneau has prepared a number of arsinic acids and finds that the parent acid of salvarsan is the least toxic.[113] On experimental trypanosomiasis, spirillosis, and syphilis, it proved to have great curative power. Although Ehrlich and Hata examined this acid and rejected it owing to the nervous symptoms it evoked, Fourneau considers this to be due to impurities. The chemotherapeutic index is equal to that of salvarsan, but the actual tolerated and curative doses are ten times as great as in the case of salvarsan, clearly an undesirable feature for clinical use.

Commercial neosalvarsans show much greater variation in composition and properties than salvarsan.[114] The examination of the distribution of sulphur and the behaviour towards iodine have contributed greatly to the elucidation of the cause of this.[115] It is due to the presence of the mono- as well as the di-formaldehyde-sulphoxylates of salvarsan in varying proportions and to the presence of uncombined sodium formaldehyde-sulphoxylate and inorganic salts. The condensation of atoxyl and formaldehyde-sulphoxylate has been described by A. Binz and E. Holzapfel.[116]

Combinations of salvarsan and neosalvarsan with mercuric chloride have been tried clinically in Germany. That the combination is a dangerous one is evident; the products have been fully investigated by Binz and H. Bauer[117] and include some toxic substances.

Of the large number of derivatives of *p*-aminophenylarsinic acid prepared and examined by the Rockefeller Institute,[118] tryparsamide, $AsO_3H_2.C_6H_4.NH.CH_2.CO.NH_2$, appears to be relatively the most favourable in its therapeutic action. Towards mice and rats infected with *Trypanosomae rhodesiense, gambiense,*[119] and *equiperdum,*[120] it has respectively the chemotherapeutic indices 1/1.5, 1/7 to 1/5, and 1/10. It has been tried clinically in the

[111] W. G. Christiansen, *J. Amer. Chem. Soc.*, 1921, **43**, 370; *J.*, 1921, 277A.

[112] *Ibid.*, 1921, **43**, 582; *J.*, 1921, 320A.

[113] *Ann. de L'Inst. Pasteur*, 1921, **35**, 571.

[114] C. Voegtlin and H. W. Smith, *J. Pharm. Exp. Ther.*, 1921, **16**, 449.

[115] G. W. Raiziss and M. Falkov, *J.*, 1921, 320A. A. D. Macallum, *ibid.*

[116] *Ber.*, 1920, **53**, 2017; *J. Chem. Soc.*, 1921, i. 30.

[117] *Z. angew. Chem.*, 1921, **34**, 1261; *J.*, 1921, 527A. *Cf.* W. Kolle, *Med. Klin.*, 1921, 1504.

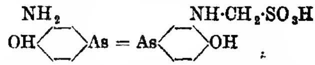
[118] *Ann. Repts.*, 1919, **4**, 501.

[119] L. Pearce and W. H. Brown, *J. Exp. Med.*, 1921, **33**, 193. *Cf.* M. Leger and E. Tejea, *Bull. de l'Inst. Pasteur*, 1921, **19**, 557.

[120] C. Voegtlin and H. W. Smith, *J. Pharm. Exp. Ther.*, 1920, **15**, 475.

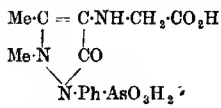
Belgian Congo on 77 human cases, no relapse occurring in some cases up to 111 days.[121]

An arsenical preparation which has an advantage over all others in that its subcutaneous or intramuscular administration is relatively painless is sulfarsenol, the essential ingredient of which is the combination of salvarsan base and formaldehyde-bisulphite :—



It was originally protected by the Germans[122] but not taken up clinically, and has now been introduced by the French. The results obtained with *spirochaeta pallida*, the organism of syphilis in man, are almost uniformly favourable.[123]

Arsenic compounds of the pyrazolone series have not hitherto been described. The lacuna is now supplied by a patent[124] which describes the preparation, for example, of the arseno-derivatives of aminoantipyrine, into the amino-group of which can be introduced the groups $—CH_2.CO_2H$, $—CH_2.SO_2H$, and $—CH_2.SO_3H$, with the production of the analogues of the salvarsan series. The products are said to be highly spirillocidal :—



Antimony and Bismuth Compounds.—The success which has attended the use of organic compounds of arsenic in medicine has not found a counterpart in the corresponding antimony compounds. The only derivative of antimony which has proved of real value is tartar emetic. It was shown by J. B. Christopherson that intravenous injections killed bilharzia in all its stages, the chitinous shell of the ovum even being permeable.[125] The successful treatment of a thousand cases of bilharziasis in Egypt by one clinic is recorded, although a desire is expressed for a somewhat less toxic substance.[126] The related bismuth compound, sodium potassium bismutho-tartrate, has recently attracted considerable notice.

[121] L. Pearce, *J. Exp. Med.*, 1921, **34**, i., 1.

[122] Meister, Lucius, und Bruning, E.P. 3615, 1912 ; *J.*, 1912, 844.

[123] Levy-Bing, Lehnhoff-Wyld and Gerbay, *Ann. Malad. Vener.*, 1919, **14**, 520. A. Mouneyrat, *ibid.*, **15**, 602. E. Chabroux, *ibid.*, 1921, **16**, 250. F. C. Doble, *Lancet*, 1920, 199, 243. E. Crawford and G. B. Fleming, *ibid.*, 1921, **2**, 700. L. W. Harrison, *ibid.*, 1921, **2**, 828.

[124] Meister, Lucius, und Bruning, G.P. 313,320 ; *J.*, 1921, 637A ; E.P. 146,870 ; *J.*, 1921, 798A.

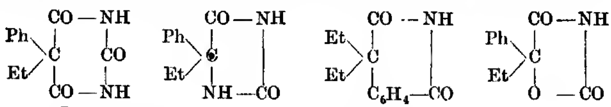
[125] *Brit. Med. J.*, 1920, **2**, 854. *Cf.* Tsykalas, *Wien. Klin. Wochsch.*, 1921, **34**, 580.

[126] F. O. Lasbrey and R. B. Coleman, *Brit. Med. J.*, 1921, **1**, 299.

B. Sauton and E. Robert showed[127] that this substance had a curative action on spirillosis. An extension to experimental syphilis in the rabbit was made by C. Levaditi and R. Saverac with equally good results.[128] The same authors have applied it to the human subject in five cases with some success,[129] and a very favourable report of 110 human cases is presented by L. Fournier and L. Guénot.[130] Unlike many of the arsenic drugs, sodium potassium bismutho-tartrate is much more toxic to spirochaetes than to trypanosomes.[131]

Hypnotics.

The presence of alkyl groups is often associated with hypnotic properties. That similarity of molecular build or arrangement may play a part may be seen by comparing the following formulæ, which represent substances possessing hypnotic and narcotic properties :—



I. II. III. IV.

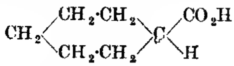
Luminal (I.) and nirvanol (II.) are well-known hypnotics. The third formula is that of diethylhomophthalimide, a member of a group of hypnotics prepared by A. Lumière and F. Perrin[132] and described in last year's report. The fourth formula is that of a diketotetrahydro-oxazole, a member of a new group of hypnotics obtained by the action of chloroformic ester on the corresponding disubstituted glycollamide. This last group forms soluble salts with alkali hydroxides or carbonates.[133] Luminal (I.) forms addition compounds with morphine alkaloids, *e.g.*, morphine, ethylmorphine, and codeine, and the products are used for inducing "twilight sleep."[134] Diallylbarbituric acid also forms similar crystalline addition compounds.[135]

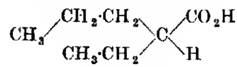
Various methods for the preparation of tho hydantoin type of hypnotic (II.) have been described previously.[136] Other avenues of approach are being systematically explored and covered by patent. Arylalkylmalononitriles, $R_1(R_2).C(CN)_2$, are treated with

[127] *Ann. de l'Inst. Pasteur*, 1916, **30**, 261.
[128] *Comptes rend.*, 1921, **172**, 1391 ; 1921, **173**, 1201.
[129] *Ibid.*, **173**, 338.
[130] *Ibid.*, 674.
[131] R. Saverac and C. Levaditi, *Comptes rend. Soc. biol.*, 1921, **85**, 430.
[132] *J.*, 1920. 762A.
[133] Soc. Chim. des Usines du Rhône, E.P. 159,153 ; *J.*, 1921, 717A.
[134] Ges. für. Chem. Ind. in Basle, G.P. 330,814 ; *J.*, 1921, 449A.
[135] *Ibid.*, G.P. 322,335 ; *J. Chem. Soc.*, 1920, i., 756.
[136] *Ann Repts.*, 1919, **4**, 498.

hypochlorite or hypobromite solutions with production of the hydantoins,[137] or urethanoarylalkylacetic acid esters of the formula $R(R_1).C(NH.CO_2R)CO_2R$ are treated with ammonia or monoalkylamines.[138]

A number of urethanes containing a chlorine atom, of the general formula, $CH_2Cl.CH_2.CHR.OCONH_2$, and others containing a phenyl group of the type $Ph.CHR.OCONH_2$ have been prepared in order to study their hypnotic properties, by J. Puyal and Mlle. Montagne.[139] The same authors in conjunction with M. E. Fourneau are examining the preparation of cyclohexanecarboxylic acid (I.) and its derivatives, as it bears a resemblance to *a*-ethylvaleric acid (II.), some derivatives of which have sedative properties.[140]


I.


II.

Chloral has been condensed with *p*-acetylaminophenol, the basal substance of a number of antipyretics. The product, $NHAc.C_6H_4.O.CHOH.CCl_3$, is said to be a more energetic soporific than chloral.[141]

Local Anæsthetics.

The possibilities of variation in the alkamine esters appears to be unlimited. *p*-Aminobenzoic acid forms the starting point for many substances with anæsthetic properties. The availability of *n*-butyl alcohol has led to the preparation of *n*-butyl *p*-aminobenzoate,[142] $NH_2.C_6H_4.COOC_4H_9$, and the general interest exhibited in allyl derivatives since J. v. Braun's discovery that N-allylnorcodeine was physiologically antagonistic to morphine, to the allyl ester of *p*-aminobenzoic acid.[143] *n*-Butyl esters of *o*-, *m*-, and *p*-amino- as well as of 2.4- and 3.5-diaminobenzoic acids have been prepared. By means of a rough test for anæsthetic power the *n*-butyl and allyl *p*-aminobenzoates and *n*-butyl 3.5-diaminobenzoate were found to be the most active.[144] A somewhat less common combination is that of *o*-diethylaminocyclohexanol and *p*-aminobenzoic acid, but its action has not yet been recorded.[145] H. Thoms and K. Ritsert have prepared a number of derivatives of

[137] Chem. Fabr. von Heyden, G.P. 335,994 ; *J.*, 1921, 601A.

[138] *Ibid.*, G.P. 335,993 ; *J.*, 1921, 601A.

[139] *Bull. Soc. Chim.*, 1920, **27**, 857 ; *J.*, 1921, 60A.

[140] *Anal. Fis. Quim.*, 1921, **19**, 192 ; *J. Chem. Soc.*, 1921, i., 566.

[141] O. Hinsberg, G.P. 332,678 ; *J.*, 1921, 370A.

[142] Soc. Chim. des Usines du Rhône, E.P. 148,743 ; *J.*, 1921, 195A. H. C. Brill, *J.*, 1921, 748A.

[143] The Abbott Laboratories, U.S.P. 1,360,994 ; *J.*, 1921, 412A.

[144] H. C. Brill, *J. Amer. Chem. Soc.*, 1921, **43**, 1320 ; *J.*, 1921, 748A.

[145] A. E. Osterberg and E. C. Kendall, *ibid.*, 1921, **43**, 1370 ; *J.*, 1921, 748A.

anæsthesin, $NH_2.C_6H_4.CO_2Et$, by introducing positive or negative groups into the amino-group.[146] The products have been tested by J. Morgenroth,[147] who found that the anæsthetic property disappeared on introducing negative groups, and that in general substitution of the amino-hydrogen atoms reduced the anæsthetic action. In one case only, that of the hydrazine, $NH_2.NH.C_6H_4.CO_2Et$, was the activity comparable with that of anæthesin.

In the well-known anæsthetic novocaine, $NH_2.C_6H_4.CO_2.CH_2.CH_2.NEt_2HCl$ the diethylaminoethyl radicle is combined with the carboxyl group. The anæsthetic properties may also appear when this radicle is introduced into the amino-group. Thus, in general, β-chloroethyldialkylamines react with p-aminobenzoic acid esters with production of β-dialkylamino-ethyl-p-aminobenzoic alkyl esters.[148] :—

$$Cl.CH_2.CH_2.NR_2+NH_2.C_6H_4.CO_2R^1 \rightarrow R_2N.(CH_2)_2.NH.C_6H_4CO_2R^1$$

The p-aminobenzoic acid esters used are methyl, ethyl, propyl, n- and *iso*-butyl, and *iso*-amyl.

A number of compounds of the novocaine type have been protected in the United States, of the general formulæ, $Ar.CO_2.(CH_2)_x.NR_2$ and $Ar.CO_2.(CH_2)_3.NRR^1$, and in particular $NH_2.C_6H_4.CO_2.(CH_2)_2.N(C_4H_9)_2$, the dibutyl analogue of novocaine.[149] The replacement of one of the ethyl groups in novocaine by unsaturated groupings, *e.g.*, allyl or styryl, leads to the production of substances with enhanced local anæsthetic properties.[150]

In the aliphatic series, E. Fourneau has prepared ethyl tetramethyldiaminohydroxyisobutyrate by the action of dimethylamine on dichlorohydroxyisobutyric acid ethyl ester. The benzoyl-derivative proved to have a local anæsthetic action but was irritant.[151]

A study of the influence of the acid radicle on the anæsthetic properties of various esters of dimethylaminodimethylethylcarbinol has been made by J. M. Cano and J. Rancedo.[152] The esters of benzoic, heptoic, and cyclohexanecarboxylic acids were of almost equal anæsthetic power, and within limits anæsthetic power increased with the molecular weight of the acid radicle.

ANTISEPTICS.

The conditions which an ideal antiseptic for use *in vivo* must fulfil are very stringent. At the present time hexamethylenetetramine is widely used to produce urinary antisepsis because it

146 *Ber. deuts. Pharm. Ges.*, 1921, **31**, 65 ; *J.*, 1921, 277A.

147 *Ibid.*

148 Soc. Chim. des Usines du Rhône, E.P. 153,827 ; *J.*, 1921, 27A.

149 The Abbott Laboratories, U.S.P. 1,358,750–1 ; *J.*, 1921, 238A.

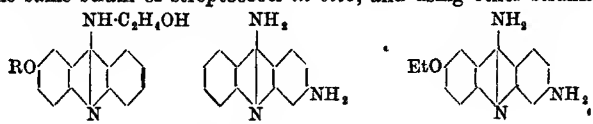
150 J. v. Braun and O. Braunsdorf, *Ber.*, 1921, **54**, 2081.

151 *Bull. Soc. Chim.*, 1921, **29**, 413 ; *J.*, 1921, 527A.

152 *Anal. Fis. Quim.*, 1920, **18**, 184 ; *J. Chem. Soc.*, 1921, i., 384.

liberates formaldehyde in the urine, but only if this is acid, a condition difficult to ensure.[153] E. G. Davis examined 204 readily accessible aniline dyes with a view to their use as urinary antiseptics.[154] Out of the 204, fifteen were chosen which were (A) antiseptic in urine, (B) excreted by the kidney, (C) relatively non-toxic. Of these only two, acri-flavine and flavine, caused the excretion of antiseptic urine after intravenous administration. The most promising groups were the triphenylmethane, xanthone, acridine, and azine groups. Acriflavine has also proved an efficient antiseptic for gonorrhœa.[155]

A valuable contribution to the chemotherapy of the acridine group has been made by J. Morgenroth, R. Schnitzer, and E. Rosenberg.[156] The order of activity towards streptococci *in vitro* of a series of acridine compounds of the type (I.) where R may be various alkyl groups, was different from the order of activity to the same strain of streptococci *in vivo*, and using other strains of



I. II. III.

streptococci, this series was inactive to many. The search for the "pantherapeutic agent" for streptococci resulted in the discovery of two very active substances (II.) and (III.), of which 2-ethoxy-6.9-diaminoacridine (III.) has been introduced as a commercial product under the name rivanol. For all strains of streptococci examined, the disinfection quotient, which is the ratio of the concentration which kills *in vitro*, to that which kills *in vivo*, was 1/2·5, which is better than that of the best previous antiseptic, vuzin (*iso*-octylhydrocupreine), which had the value 1/5. Against staphylococcus the quotient is even better, being 1/1.

J. B. Cohen and C. H. Browning have also examined the chemotherapy of acridine compounds with special reference to pyogenic infections.[157] The chemical fragments of the acridine molecule, such as pyridine and quinoline derivatives, were of low-grade antiseptic power, and in the acridine series substances with free amino-groups were the most efficient, the methylation of the tertiary nitrogen atom 10, having no effect. In the phenazine series, *i.e.*, derivatives of $C_6H_4:N_2:C_6H_4$, the methochloride of, for example, 2.7-diamino-3.6-dimethylphenazine and 2-amino-naphthyl-7-amino-3-methylphenazine were as powerful antiseptics

[153] L. J. Henderson and W. W. Palmer, *J. Chem. Soc.*, 1913, i., 558.

[154] *Amer. J. Med. Science*, 1921, **161**, 251.

[155] D. Watson, *Brit. Med. J.*, 1919, **1**, 571.

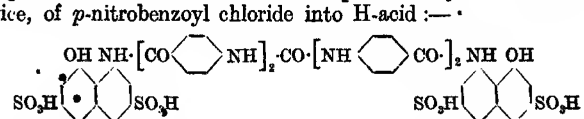
[156] *Deut. Med. Wochsch.*, 1921, **47**, 1317.

[157] *Brit. Med. J.*, 1921, 2, 695.

towards *staphylococcus aureus* as the acridine series. The action of similar members of the acridine series on protozoa has been investigated by E. Lenz[158] and the bactericidal action of gold, silver, and cadmium compounds of flavine by M. Berliner.[159]

For an antiseptic to be effective against typhoid carriers, it should be excreted through the gall-bladder and not in the urine. A number of dyes were examined and found active *in vitro* against *B. typhosus*, but were not excreted through the gall-bladder. New Fast Green 3B, a triphenylmethane derivative, proved effective in rabbits, being excreted in the bile; it may, however, be toxic.[160]

Bayer 205. A new era in trypanosoma therapy seems to have opened up with the introduction of this substance. Ehrlich and Shiga[161] showed that Trypan Red, a dye produced by coupling a diazotised benzidinesulphonic acid with a disulphonic acid of β-naphthylamine, had pronounced trypanocidal properties. Following up this discovery Mesnil and Nicolle examined the trypanocidal action of a number of dyes containing as an essential constituent an aminonaphthalenesulphonic acid.[162] As a result it was recognised that the dyes which had the greatest trypanocidal power were derivatives of naphthalene containing sulphonic acid groups in the positions 3.6 and hydroxy, amino, aminohydroxy, dihydroxy, and diamino-groups in the positions 7 and 8. The most favourable substance was prepared by the Bayer firm by coupling diazotised *p*-diaminodiphenylurea with H-acid (1.8-aminonaphthol-3.6-disulphonic acid). A great advance was the discovery by the same firm that the trypanocidal substance need not be a dye, and this firm has protected by patent a large number of ureas derived mainly from nuclei containing amino-sulphonic acids of naphthalene.[163] As an example of the type of substance produced may be quoted the urea, formed by the action of carbonyl chloride on the corresponding amino-derivative of the substance produced by the introduction twice, of *p*-nitrobenzoyl chloride into H-acid :—



The variations that have been protected are many. H-acid may be replaced by a great variety of other amino-di- and trisulphonic acids with or without hydroxy, methoxy, chlorine, or

[158] *Z. ges. Exp. Med.*, **12**, 195; *J. Chem. Soc.*, 1921, i., 756.

[159] *Berl. Klin. Woch.*, 1921, **58**, 177; *J.*, 1921, 486A.

[160] T. D. Beckwith, *J. Inf. Dis.*, 1921, **29**, 495.

[161] *Berl. Klin. Woch.*, 1904.

[162] *Ann. Inst. Pasteur*, 1906, **20**, 417, 519.

[163] G.P. 278,122, 284,938, 288,272, 288,273, 289,107, 289,163, 289,270, 289,271, 289,272, 291,351; *J.*, 1914, 825; 1915, 347, 889; 1916, 438, 654; 1918, 20A.

bromine atoms. The acid chloride which is introduced once, twice, or more times into the amino-group, can also be varied and may be, for example, *m*- or *p*-nitrobenzoyl, *m*-nitroanisoyl, *m*-nitrophenylsulphonyl, *p*-nitrophenylacetyl, *m*-nitrocinnamoyl, and similar radicles of the naphthalene series. The CO group which links the two halves of the molecule may be replaced by CS forming thioureas. The formation of mixed types is also patented and also the replacement of the aminonaphthalenesulphonic group by derivatives of benzene or carbazole, the therapeutic activity of the benzene derivatives being only manifested if twice substituted by the acid chloride. Finally the NH.CO group which links the nuclei together may be replaced by the urea group NH.CO.NH. The claim is made that all these substances in dilute solution cause the disappearance of spirochaetes from the blood of infected animals and have a powerful healing action on animals with trypanosomiasis.

Bayer 205, the exact composition of which is at present a trade secret, appears to belong to the above group. It is a white powder, soluble in water even to 20% forming a neutral solution which can be sterilised and keeps well. Several observers in Germany have recorded its curative action[164] on mice, rats, rabbits, and guinea-pigs suffering from *Trypanosomæ brucei*, *equinum*, *equiperdum*, *gambiense*, and *rhodesiense*. Its chemotherapeutic index is especially favourable and the substance may be administered orally, subcutaneously, or intravenously. It does not kill trypanosomes *in vitro*, but renders them incapable of multiplying when injected into animals. The serum of animals or of normal men who have received the substance intravenously or orally remains active for many days and when injected can cure animals suffering from trypanosomiasis. Animals which have been cured are immune from re-infection for some considerable time. Owing to lack of opportunities it has, so far, only been tried on two human cases of sleeping sickness, with successful results in one case, the details of which have recently been published.[165] A German expedition, however, under the auspices of the British Colonial Office, is on its way to Rhodesia to test the treatment.[166] In England the curative action on animals has been confirmed by C. M. Wenyon.[167]

[164] L. Haendel and K. W. Joetten, *Berl. Klin. Wochsch.*, 1920, **35**, 821; M. Mayer and H. Zeiss, *Arch. f. Schiff. Trop. Hyg.*, 1920, **24**, 257; 1921, **25**, 149, 259. *Cf. also ibid.*, 29; H. Miessner and R. Berge, *Bull. Inst. Pasteur*, 1921, **19**, 380. W. Walther and W. Pfeiler, *ibid.*, 380.

[165] P. Mühlens and W. Menk, *Münch. Med. Wochsch.*, 1921, **46**, 1488.

[166] *Lancet*, 1921, **2**, 1926.

[167] *Brit. Med. J.*, 1921, **2**, 747.

PHOTOGRAPHIC MATERIALS AND PROCESSES.

By F. F. Renwick, A.C.G.I., F.I.C.

The first steps towards the achievement of photography as a practical art were largely due to men of acknowledged scientific repute of British birth. The names of Josiah Wedgwood, Sir John Herschel, Sir Humphrey Davy, Henry Fox Talbot, and Robert Hunt readily occur to the mind as distinguished men of science who devoted considerable attention to the subject in the first half of last century. Herschel, Fox Talbot, and Hunt all added considerably to the list of known photochemical reactions, and to Fox Talbot belongs the distinction of working out more than one process to a successful issue and of introducing the method of producing positive prints from a negative and so enabling the production of any number of copies. It is highly fitting therefore that the Royal Photographic Society should recently have undertaken the guardianship of Fox Talbot's apparatus and results and the setting up of a permanent memorial to him.

Towards the end of last century, after the establishment of numerous firms for the wholesale manufacture of sensitive materials, very few men of note in the scientific world devoted themselves to the study of photochemical problems in spite of their profound importance and interest, but the death, at the close of last year, of Sir Wm. de W. Abney removes from our midst one whose name will always be associated with his valuable contributions to photographic science which traversed a very wide field both in the chemical and the physical aspects of the subject.[1]

The present flourishing photographic industry owes its development almost entirely to the dogged energy and perseverance of a number of untrained enthusiasts whose names are mostly unknown to scientific men, and it is probable that in the whole world there were not a score of well-trained chemists employed in it thirty years ago.

The present outlook is very different. In the first place the industry has absorbed and trained a considerable number of young men who had first received an education in scientific method and who have elaborated Hurter and Driffield's invaluable system of examining and classifying photosensitive materials, so that to-day

[1] Sir W. Abney, *Phot. J.*, 1921, 61, 44, 296.

quantitative modes of expression are, or should be, regularly employed by all serious workers to describe their attributes.

Secondly, the industry has become so huge and complex that it would be impossible to produce the required quantities and the variety of these very delicately balanced products with reasonable uniformity without an elaborate system of scientific control. (In illustration of the magnitude of the industry the following figures are instructive. Approximate number of kinema theatres in existence 90,000; estimated length of kinema film exhibited every week 300,000 miles, of which at least 10,000 miles represents entirely new matter, no allowance being made for the enormous amounts consumed which are never issued for exhibition. To this must be added all the roll films and plates and the positive printing materials of all kinds used in other photographic work, both professional and amateur.)

Thirdly, as a consequence perhaps of the industrial difficulties which have arisen since the war, there is a keener appreciation of the overwhelming importance of light as the prime cause of those innumerable natural synthetic and analytic reactions on which all living matter depends for its growth and development, and as a result we observe a great revival of interest in the mechanism of photochemical changes and a desire to direct and control them for the service of mankind. It has become evident that efficient photochemical manufacturing processes would save the community the expenditure of much manual labour and postpone the depletion of our rapidly dwindling and irreplaceable supplies of coal and oil. Moreover, if such processes can be colour-sensitised effectively there seems less reason to assume they would require to be carried on in tropical climates to be economically successful.

Photography then, should be regarded as merely the first photochemical industry to be established, and as such it cannot fail to benefit from the researches in other branches of photochemistry, the study of catalytic reactions, and particularly from investigations of heterogeneous reactions in colloidal media which appear in the future.

As evidence that British photographic chemists are alive to the importance of widening their outlook, the appearance of a new journal published by the Scientific and Technical Group of the Royal Photographic Society under the title "Photographic Abstracts" is a most welcome sign and deserves the support of all serious workers in the subject. The enlightened policy of those firms who jointly bear the greater part of the cost of this publication is highly praiseworthy and cannot fail to be rewarded through the greater zeal for and efficiency in the performance of their duties which it will surely evoke among their technical staffs.

Photography has undoubtedly regained much of its popularity as a pastime, and the lure of the kinema theatre seems irresistible to the majority; moreover the employment of photomechanical processes for illustration work continues to grow steadily, while professional and scientific photography continue rapidly to multiply their already numerous ramifications, so that if a reasonably early return to normal trading conditions should occur it is safe to predict a considerable permanent expansion of the industry. There is a far wider and more intelligent appreciation of the advantages of colour-sensitive negative-making materials for all kinds of work than before the war, probably as a consequence of the large numbers of men who learned from experience on active service how indispensable such plates were to our success. There are indications of a desire on the part of manufacturers to simplify their problems by producing only a few articles in large quantities, but it has long since been found impossible to produce even one product which suits all tastes, so many and so subtle are the requirements of different users.

While the importance of photography in everyday life is but dimly realised by the general public, few even among the highly-educated classes realise what an effect it has had on man's intellectual life during the past two years. But for the fact that a few star images occupied certain positions on a few photographic plates exposed at the solar eclipse in 1919, it is certain that the majority of us would have taken no interest in theories of relativity. An attempt to verify these observations on Christmas Island in the Indian Ocean and elsewhere at the eclipse next September is already organised and will again rely on photographic records of apparent star positions, when doubtless there will follow another flood of ideas on this abstruse subject. In delicate work of this character careful attention must be paid to various disturbing factors such as the mutual influence of adjacent images—a subject recently re-studied by F. E. Ross.[2]

During the past year the photographic industry has suffered from the prevailing world-wide trade depression, though perhaps less acutely than most. There was a marked fall in the prices of fine chemicals during the summer months, but this advantage may be lost, presumably to the benefit of the fine chemicals trade of this country, by the operation of the Safeguarding of Industries Act, 1921, which came into force on October 1st last, since every fine chemical and almost all the apparatus used in the industry fall within its scope.

At the date of writing, the depreciated value of the German mark apparently outweighs any encouragement which the Act might have given to our fine chemicals industry, while this measure

[2] F. E. Ross, *Astrophys. J.*, 1921, **53**, 349.

certainly makes the obtaining of rare synthetic chemicals from abroad an extremely aggravating process.

Raw Materials.

Among the raw materials of the photographic industry, the three which call for the greatest care, judgment, and experience in their selection and use are gelatin, paper, and collodion cotton. There are no generally recognised methods of testing any of these products for photographic purposes except the obvious one of trying them on a small scale and noting the results before proceeding to large-scale use, and it must be admitted that at present there seems little prospect of devising really reliable chemical methods of testing them.

It is satisfactory to be able to record that considerable progress has been made in this country and elsewhere during and since the war in the production of first-class gelatins suitable for all photographic purposes, and we are now quite independent of Germany in this matter.

Regarding paper stock suitable for bearing sensitive emulsions, some progress has also been made, but of a more limited character. Supplies of collodion cotton of British manufacture suitable for preparing print-out collodion emulsions are also more easily obtainable than in pre-war days.

While a great deal of new work on gelatin has been published during the past year, a proper appreciation of the bearing of modern research in this field on photographic problems is as yet impossible. It becomes daily clearer, however, that there are numerous facts, with which most photographic works chemists are familiar in practice, whose interpretation is rendered easier by the aid of the newer theories dealing with colloidal forms of matter, and it is to be hoped that the photographic industry will derive some benefit by the adoption of the methods of examining gelatin which are gradually being worked out.[3] In many cases, however, these are little more than slight modifications of old physical tests which have been long since found to be of no great assistance to the emulsion maker.

What is urgently needed as a beginning is a satisfactory method of determining the relative proportions and characteristics of the hydrolysed and unhydrolysed constituents of commercial gelatins. A ready means of separating them unchanged would enable their separate influences on emulsion-making processes to be properly studied, and the diverse photographic qualities of

[3] S. E. Sheppard and S. S. Sweet, *J. Amer. Chem. Soc.*, 1921, **43**, 539. H. D. Dakin, *J. Biol. Chem.*, 1920, **44**. 499; *J.C.S.*, 1921, **120**, i., 66. S. E. Sheppard and S. S. Sweet, *J. Ind. Eng. Chem.* 1921, **13**, 423. S. E. Sheppard and F. A. Elliott, *J. Amer. Chem. Soc.*, 1921, **43**, 531.

different brands of gelatin to be correlated with their chemical as well as their purely physical differences. Moeller's recent studies[4] of Procter's discovery that the addition of a little acid precipitates dissolved gelatin from saturated solutions of common salt leaving the degradation products in solution, appears to offer an opening for attacking this problem.

Several new patents for flexible supports of a non-inflammable character have been granted,[5] but from one cause or another the proportion of positive film of the "non-flam" type shown in picture theatres is still quite small, hence it would seem that the ideal support is still to seek.

Storage of Sensitive Materials.

One of the most intricate problems constantly confronting the manufacturer of light-sensitive materials is the preservation of their properties unimpaired up to the time of use—a period which may amount to several years, under the most varied climatic and other conditions of storage. The problem presents two essentially different aspects; firstly, the exclusion, by the use of more or less impermeable wrappings, such as sealed tins, foils, waxed papers, etc., of moisture and injurious gases or vapours, and secondly, the discovery of stabilising agents or of improved processes of manufacture which will arrest or minimise any tendency to spontaneous changes in the sensitive materials themselves. Naturally enough, discoveries falling within the second category are not usually published but become jealously guarded trade secrets, so that the chemistry of stabilisers is an almost unexplored field of scientific enquiry.

A novel mode of protecting a photographic film against moisture has been patented by F. W. Lovejoy,[6] who applies to the surface a transparent layer of a fatty acid (palmitic or stearic) which is saponified and dissolved by the alkali of the developer. E. Merck and L. Weber[7] claim the addition of certain salts, *e.g.*, ammonium oxalate or acid phosphate, to the sensitising ferric oxalate preparation for improving the keeping quality of negative tracing (blue print) papers. A report by the Eastman Kodak Company[8] deals with the fading of finished prints made by the same process and recommends that instead of plain water, a 0·2% potassium ferricyanide solution be used for development. It condemns the

[4] W. Moeller, *Kolloid-Zeits.*, 1921, **28**, 281; **29**, 45.

[5] F. Schaurich, *Kunststoffe*, Nov., 1920, 207. S. H. Wood, U.S.P. 1,364,342; *J.*, 1921, 164A. H. Dreyfus, U.S.P. 1,353,384-5. G. W. Miles, E.P. 146,212.

[6] F. W. Lovejoy, U.S.P. 1,342,590; *J.*, 1921, 164A.

[7] E. Merck and L. Weber, G.P. 331,745; *J.*, 1921, 335A.

[8] *Eastman Kodak Lab. Rep.* No. 1091; *Phot. Abst.*, 1921, No. 346.

practice of adding hydrogen peroxide to the development water as conducive to rapid fading.

Before proceeding to deal with the more usual chemical and photochemical side of photography two very ingenious inventions must be mentioned.

The first is Louis Lumière's method[9] of producing a composite photograph giving a very satisfying illusion of solidity (photo-stereosynthesis). He prepares a number of positive transparencies on glass, each of which depicts sharply a slightly different plane of the object, other planes being thrown out of focus by special optical devices during the making of the original negatives. These transparencies must be properly spaced in due order one behind another, in a framework lighted from the rear and viewed normally to secure the desired effect.

The second is H. M. Edmunds' invention enabling relief models in wood, ivory, etc., to be produced mechanically from a photograph (photosculpture).[10] A spiral pattern is projected optically on to the sitter's head and shoulders and appears on the photograph as a close series of contour lines. A special machine is employed to translate the motion of a stylus along these contour lines into the appropriate motion of a cutting tool on the block of material employed. The results shown in last year's photographic exhibitions are certainly very interesting.

Aviation has led to the development of new and important applications of photography to surveying and map-making from aerial photographs. The progress already made in this highly technical subject has been ably reviewed by L.-P. Clerc.[11]

KINEMATOGRAPHY.

Kinematography has reached such enormous dimensions that it must now be regarded as a separate industry of a highly complex character, which uses huge quantities of sensitised negative and positive film as its chief raw materials, rather than as a branch of photography. Nevertheless, any further improvements in these raw materials must depend on the chemists and emulsion makers in the photographic industry and will naturally find many other fields of application, but such progress is necessarily rather slow. The energies of research workers in kinematography are mainly devoted to the solution of optical and mechanical problems with which this report does not profess to deal.

[9] L. Lumiere, *Comptes rend.*, 1920, **171**, 891; *Brit. J. Phot.*, 1921, **68**, 110; *Bull. Soc. Franç. Phot.*, 1920, **7**, 262.

[10] L.-P. Clerc, *Phot. J.*, 1921, **61**, 381.

[11] H. M. Edmunds, *Amat. Phot.*, 1921, **52**, 189; E.P. 170,685.

It is of interest, however, to note that inventors appear to be chiefly engaged on four problems :—

1. The elimination of the disadvantages arising from the intermittent projection and the discontinuous motion of the film through the projector. A large number of devices permitting continuous motion of the train of pictures has been patented[12] and some of them publicly exhibited, so that it may not be long before flicker, underlighting, film breakage, and other evils will be things of the past.

2. The discovery of a satisfactory method of imparting the appearance of stereoscopic relief to motion pictures.[13]

3. The perfection of a simple means of synchronising sound records and motion pictures—a feat which was shown to be possible in skilled hands with separate gramophone and kinema records at the Brussels International Congress of Photography in 1910.

Recently, however, considerable success has attended efforts to combine both the picture and the sound record on one film. Variations in opacity in the photographic sound record cause rapid fluctuations in the intensity of an electric current passing through some form of light-sensitive cell, and these operate suitable amplifying telephonic devices for reproducing the original sounds.[14]

4. The production of satisfactory motion pictures in natural colours.[15]

In regard to this long-sought goal it appears fairly certain that for some time to come a two-colour system, in spite of its serious limitations, is more likely to be a commercial success than a three-colour method, since the latter inevitably offers far greater technical difficulties. Modern developments indicate that a practical solution is likely to be found first either in a method by which each unit picture on the film is a composite record in colour which can be used in existing projectors without alteration, or by one of the optical methods enabling the simultaneous making of the two records on adjacent areas of one film through a single lens and

[12] K. Higginson, E.P. 165,114 and 165,487; see also *Phot. J.*, 1921, **61**, 261. C. H. Claudy, *Scient. Amer.*, 1921, **124**, 288, 297, 299. C. Zeiss, E.P. 146,209. Petra A.-G., E.P. 154,873. W. C. Plank, U.S.P. 1,366,488. M. F. and L. D. Hill, U.S.P. 1,367,475. E. H. Lysle, U.S.P. 1,367,487-8. J. A. Perry, F.P. 512,298. O. Messter, G.P. 331,550 and 332,273. C. W. R. Campbell and F. G. A. Roberts, E.P. 161,329. E. Mechan, F.P. 516,277.

[13] R. Gantes, F.P. 507,633. J. L. Pech, *Scient. Amer. (Monthly)*, 1921, 531; *La Nature*, 1921, **49**, 75. L. L. Ruffier, E.P. 152,367. F. N. Hallet, U.S.P. 1,363,249. A. d'Halloy, F.P. 514,076. S. Türk, G.P. 334,383. A. F. Boorman, E.P. 165,587.

[14] L. A. Collins, U.S.P. 1,366,446; *Times*, Sept. 24 and 28, 1921; *Nature*, 1921, Oct. 27, p. 276.

[15] Natural Colour Pictures Co. (W. F. Fox), E.P. 143,180. E. C. S. Parker, E.P. 507,724. I. Furman, U.S.P. 1,371,969 and 1,371,970.

projection through two adjacent colour filters to combine on the screen.

An interesting short discussion of the various systems of colour kinematography theoretically possible, which contains some very decided expressions of opinion concerning them, is to be found in an article recently published by A. Gleichmar.[16] He rules out as unworthy of consideration all two-colour systems and states clearly but briefly the demerits and inherent difficulties of each of the methods available to experiment. An article by C. E. K. Mees in *The Photo Miniature* for July, 1921, also contains interesting expressions of opinion on the subject.

The only process of colour kinematography to come on the British market during the year is the American one "Prisma," made under W. V. D. Kelley's patents.[17] It is a two-colour process in which the picture is composed of juxtaposed microscopic areas of orange-red and blue-green, made by dye-toning on either side of a double-coated film. A short film based on a three-colour subtractive process by S. M. de Procoudine-Gorsky[18] was exhibited privately in London last spring.

In connexion with processes of staining up the positive colour records, considerable attention is being devoted to the dye-adsorptive properties of the silver halides and metallic ferrocyanides,[19] while a novel property of the developed silver image forms the basis of a patent by J. H. Christensen,[20] who finds that in the presence of suitable reducing agents (*e.g.*, amidol or hydrosulphites) certain dyes are readily reduced to their leuco bases where the silver image occurs. An interesting reaction of a similar kind is described by J. I. Crabtree[21] who finds that even an ordinary acid "hypo" fixing bath can function as the reducing agent.

Colour Photography.

In a chapter of J. Plotnikow's recently published book on "Photochemistry"[22] appears the only important new suggestion of a possible method of recording colour photographically. He points

[16] A. Gleichmar, *Phot. Ind.*, 1921, 894.

[17] W. V. D. Kelley, E.P. 129,638; *Brit. J. Phot.*, 1920, **67**, *Col. Suppl.*, 47; 1921, **68**, *Col. Suppl.*, 18.

[18] S. M. de Procoudine Gorsky, E.P. 135,171 and 168,100. See also *Brit. J. Phot.*, 1921, **68**, *Col. Suppl.*, 38.

[19] A. Traube, E.P. 147,005 and 147,103; *J.*, 1921, 325A, 413A. F. E. Ives, *Brit. J. Phot.*, 1921, **68**, *Col. Suppl.*, 3; *J.*, 1921, 99A; *Brit. J. Phot.*, 1921, **68**, 186; *J.*, 1921, 325A. L. Lobel, *Bull. Soc. Franç. Phot.*, 1921, **8**, 78. W. V. D. Kelley, E.P. 160,137. J. I. Crabtree, U.S.P. 1,389,742; *J.*, 1921, 791A. S. M. de Procoudine Gorsky, E.P. 168,100.

[20] J. H. Christensen, E.P. 133,034; *J.*, 1921, 164A.

[21] J. I. Crabtree, *Brit. J. Phot.*, 1921, **68**, 32; *J.*, 1921, 129A.

[22] J. Plotnikow, "*Allgemeine Photochemie.*" See also *Phot. Ind.*, 1921, 6.

out that if dyes could be made which were "fast" to the acid constituents of the atmosphere and to light except in the presence of a colourless catalytic agent, in the presence of which they change, on exposure, to stable colourless products, removal of the catalyst after printing would yield a permanent coloured image. No such combinations of dye and catalyst are, however, known at present.

Apart from this suggestion no new principle appears to have been evolved, and most of the published papers and patents are concerned either with means of overcoming well-known mechanical difficulties or refer to special toning or dyeing operations in which one or other of the known properties of selectively hardened gelatin, or of the silver image or an insoluble salt formed from it, is employed as medium for the colour.[23]

There can now be little doubt that no process involving the use of more than one plate for negative making is likely to attract the general public. This part of the problem may be said to have been solved by such screen-plate processes as the Autochrome and Paget colour processes. They remain, however, comparatively little used, largely owing to the absence of a simple method of reproducing them in the form of coloured prints on paper. Here again it is probably safe to hazard the opinion that any system involving the making of a colour analysis of the original and a separate printing on paper from each of the three negatives so obtained would never achieve popularity. Hence all methods based on the superposition of dyed reliefs or on the transfer of dyes to paper to form the print by imbibition from three separate stained-up copies must give way to any successful method of producing the coloured paper print from a single printing plate. An interesting historical survey including some of the former processes is contained in two recent articles by E. J. Wall,[24] while in connexion with the possibility of successfully reproducing screen-plate transparencies on paper from a single printing plate the patent of O. Fielitz[25] is worthy of attention.

COLOUR SENSITISERS AND DESENSITISERS.

While the photographic industry shares with most others the need, for tinctorial purposes, of a range of dyes which are fast to light and various chemical reagents, and which are adsorbed by certain materials and not by others, it is peculiar in requiring dyes having the power to modify the normal blue-violet sensitiveness of the silver halides by conferring upon them a high degree of sensitiveness to other regions of the spectrum. Some are required

[23] Ges. f. angew. Phot. m.b.H., G.P. 328,618; *J.*, 1921, 196A. B. Lincke and R. Kaufhold, G.P. 336,041; and see also ref. 19.

[24] E. J. Wall, *Brit. J. Phot.*, 1921, 68, *Col. Suppl.*, 30, 34.

[25] O. Fielitz, F.P. 515,067.

to sensitise over a quite limited range of wave-lengths, others for as large a range as possible, and all are desired to operate without depressing the white-light sensitiveness of the emulsion or inducing chemical fog or other defect. The discovery and study of sensitising dyes is an almost limitless and singularly attractive field of investigation which in recent years has received considerable attention in this country, in France, and the United States, instead of being left almost entirely to German chemists, as had been the case for some years before the war.

Two new methods of preparing plates highly sensitive in the ultra-violet have been described by J. Duclaux and P. Jeantet.[26] In one case the surface of an ordinary gelatinobromide plate is coated, before exposure, with a thin film of an oil or other liquid which does not penetrate the gelatin but which fluoresces strongly in ultra-violet light. After exposure this liquid is washed off in a suitable solvent before development is proceeded with.

According to the second method, an ordinary dry plate is treated in a horizontal position with sulphuric acid of sufficient strength to dissolve the gelatin. The silver salts settle on to the glass and are washed free from gelatin and acid in a sluggish stream of water, dried, and finally protected by a thin coating of collodion before exposure. Such plates are stated to be highly sensitive to ultra-violet radiation even beyond 1900 A.U.

It is apt to be overlooked that even the fastest modern dry plates do not fully utilise the normal sensitiveness of silver bromide because of the high opacity of gelatin and of our glass lenses to short-wave ultra-violet light. With such plates as those described above it would be very interesting to investigate the possibilities of utilising as sensitisers colourless substances having absorption bands in the ultra-violet region.

Even the most satisfactory colour sensitisers known are far from enabling us to utilise the incident light energy in other regions of the spectrum so efficiently as the undyed plate utilises the blue-violet. As a matter of practical experience it has been found extremely difficult to increase the total sensitiveness to bright daylight of a rapid dry plate by colour-sensitising it, the added sensitiveness to longer wave-lengths being always accompanied by a fall in blue-sensitiveness. That this result is not due to any direct antagonism between lights of different colours when operating simultaneously is negatived, not only by giving equal exposures in a spectrograph to plates of the same batch, both undyed and dyed, and comparing the effects in the blue, but by a recent communication of F. C. Toy,[27] who finds the effects of differently-coloured lights acting together to be simply additive. At present

[26] J. Duclaux and P. Jeantet, *J. de Physique*, 1921, **2**, 156.

[27] F. C. Toy, *Proc. Roy. Soc.*, 1921, A **100**, 109.

it remains obscure why we are unable enormously to increase the sensitiveness to white light of fast emulsions by colour-sensitising them. With very slow, fine-grained emulsions it is quite easy to accomplish this, as most practical emulsion makers have long known, but the point has been emphasised very usefully, and amply illustrated, in papers by Lüppo-Cramer[28] during the past year.

For some time two or three dyes have been known (Pinachrome Violet, Sensitol Violet) which operate without reducing, if they do not enhance, the total sensitiveness of rapid plates to white light, but they are very prone to cause fog and are otherwise difficult to handle. During the year a new and powerful green-sensitiser, said to be a basic dye of an entirely new class, has been put on the market by the firm of Meister, Lucius, u. Brüning under the name Pinaflavol. It confers sensitiveness throughout the green extending to the D (sodium) lines and shows no depression of sensitiveness in the blue-green as do dyes of the Eosin class. Like those already mentioned, it has the unusual property of enhancing rather than diminishing the total sensitiveness of the plate, but unfortunately it also readily gives rise to chemical fog and shortens the useful life of plates treated with it.[29] Another dye of the same type has been examined and reported on by Lüppo-Cramer under the designation P2 showing these qualities in a still greater degree. Incidentally he makes several interesting observations on the different effects of chemical and physical development in such cases, no chemical fog being obtained by the latter method of development, and a greater relative increase of sensitiveness being found. Other papers by the same author[30] dealing with the colour-sensitising of silver iodide contain a number of curious and interesting observations.

Patents have been granted to E. Q. Adams and H. L. Haller for sensitising dyes of the dicyanine class produced by the action of alcoholic solutions of strong bases upon the alkyl iodides of lepidine.[31] Miss F. M. Hamer has prepared and systematically studied a large group of isocyanine dyestuffs containing the amino, acetylamino, or cinnamoylamino groups in all practicable positions in the molecule and has drawn conclusions concerning the influence of these groups and their positions in the molecule on sensitising properties.[32]

[28] Lüppo-Cramer, *Die Phot.*, 1921, Nos. 6 and 8; *J.*, 1921, 750A. *Phot. Ind.*, 1921, 417. *Der Phot.*, 1921, **31**, 242.

[29] Lüppo-Cramer, *Der Phot.*, 1921, **31**, 281.

[30] Lüppo-Cramer, *Phot. Ind.*, 1921, 611, 669; *Die Phot.*, 1921, Nos. 6 and 8; *J.*, 1921, 750A.

[31] E. Q. Adams and H. L. Haller, U.S.P. 1,374,871-2; *J.*, 1921, 413A.

[32] F. M. Hamer, *Chem. Soc. Trans.*, 1921, **119**, 1432; *J.*, 1921, 791A.

In a paper by W. König and O. Treichel[33] dealing with the constitution of the cyanines and isocyanines the authors abandon König's earlier view that in preparing these dyes one of the quinoline rings has suffered fission of the pyridine ring, the reason being that compounds of this type, when prepared, failed to show the characteristics of the isocyanines. The paper contains, besides, descriptions of a series of condensation products of dimethylaminobenzaldehyde and dimethylaminocinnamaldehyde with α and γ methyl cycloammonium salts, which it would be interesting to examine for sensitising properties in view of Mills and Evans' negative result with *o*-aminocinnamylidenequinaldine (see *Ann. Repts.*, **5**, 116).

Confirmation of the writer's observation of red sensitiveness conferred by the action of soluble iodides upon silver bromide emulsions is forthcoming in a paper by R. B. Archey[34] and in one which will shortly appear in the *Photographic Journal* by S. E. Sheppard, who, however, finds the effect not to be common to all emulsions.

A very considerable amount of attention has been devoted to the study of desensitising materials which have now found a useful field of application in practical photography. Prior to Lüppo-Cramer's discovery of the utility of the safranine dyes as desensitisers which do not impair the latent image, this class of substances was regarded simply as an unmitigated nuisance to the manufacturers and users of photosensitive materials since they are of fairly widespread occurrence and readily give rise to insensitive spots and markings on their products. Lumière and Seyewetz[35] have studied a large range of dyes and other materials for desensitising properties and find Aurantia (ammonium salt) sufficiently powerful for desensitising Autochrome plates and preferable to phenosafranine on the ground of the greater ease of removing the dye afterwards. Lüppo-Cramer[36] has actively pursued the subject and concludes that desensitisers act as mild oxidising agents in preventing the formation of a latent image. As might have been expected, in view of the known depressant action of many colour-sensitisers, it has been found that phenosafranine and some other desensitisers can exert a colour-sensitising influence.[37]

[33] W. König and O. Treichel, *J. prakt. Chem.*, 1921, **102**, 63; *J.C.S. Abst.*, 1921, **120**, 738.

[34] R. B. Archey, *Phot. J.*, 1921, **61**, 235; *J.*, 1921, 413A.

[35] A. and L. Lumière and A. Seyewetz, *Brit. J. Phot.*, 1921, **68**, 351; *J.*, 1921, 529A. *Brit. J. Phot.*, 1921, **68**, *Col. Suppl.*, 29; and *Bull. Soc. Franç. Phot.*, 1921, **8**, 216; *J.*, 1921, 718A.

[36] Lüppo-Cramer, *Phot. Ind.*, 1921, 259, 312, 669; *J.*, 1921, 325A. *Die Phot.*, 1921, No. 3, 1; No. 4, 18. *Phot. Rund.*, 1921, 37; *J.*, 1921, 324A.

[37] Lüppo-Cramer, *Phot. Ind.*, 1921, 417.

Photographic Developers and Development.

There have been no important additions to the already large assortment of available developing agents during the year. Patents have been granted to E. Kolshorn [38] for derivatives of *p*-aminophenol and its O-alkyl ethers, to A. S. McDaniel and A. H. Nietz [39] for the use of diaminophenolsulphonic acid in alkaline solution, and to J. Hauff u. Co.[40] for *o*- and *p*-amino and diaminophenol and cresolsulphonic acids in alkaline solution.

W. Ermen[41] has made some interesting comparisons of the relative rates of exhaustion of a number of developers in equal concentrations, the results showing clearly that the price per ounce is a very imperfect criterion of the real cost of a developing agent when it is used economically and in quantity. In a series of articles B. T. J. Glover [42] discusses the application of the Watkins factorial method of the development of plates and papers; one of the most important points emphasised is that for bromide papers there is a certain range of correct exposures within which identical prints are obtainable by compensatory alterations in the length of development.

The important question of preserving developing solutions from atmospheric oxidation continues to receive attention, the most interesting contributions being M. J. Desalme's method[43] of preserving amidol by means of a complex stannous tartrate solution, and L. J. Bunel's method by means of lactic acid,[44] which are both fairly effective. Unfortunately they do not obviate the indelible black stain which amidol imparts to the fingernails on prolonged working with this developer.

To Lüppo-Cramer[45] are due some further interesting observations on the increased rapidity of action of quinol (hydroquinone) developers in the presence of traces of phenosafranine. He recommends this mixture as a cheap developer of the rapid class and ascribes the previously observed similar effect of mere dilution in the case of amidol and several other developing agents to the liberation of the free base by hydrolysis and its adsorption by the silver halide.

[38] E. Kolshorn, E.P. 145,614, 155,575, 155,576; *J.*, 1921, 369A.

[39] A. S. McDaniel and A. H. Nietz, U.S.P. 1,370,896; *J.*, 1921, 325A.

[40] J. Hauff u. Co., G.P. 327,111, 328,617, and 333,687; *J.*, 1921, 371A, 603A.

[41] W. Ermen, *Brit. J. Phot.*, 1921, **68**, 64; *J.*, 1921, 163A.

[42] B. T. J. Glover, *Brit. J. Phot.*, 1921, 503, 519.

[43] M. J. Desalme, *Rev. Franç. Phot.*, 1921, **2**, 128, 130; *J.*, 1921, 529A.

[44] L. J. Bunel, *Bull. Soc. Franç. Phot.*, 1921, **8**, 290. L. Lobel, *ibid.*, **8**, 291.

[45] Lüppo-Cramer, *Der Phot.*, 1921, 65; *J.*, 1921, 280A. *Kolloid-Zeits.*, 1921, **28**, 174; *J.*, 1921, 324A. *Phot. Korr.*, 1921, **58**, 121. *Phot. Ind.*, 1921, 912.

The subject of chemical fog, its relation to sensitiveness, and the causes which give rise to it, is one of very great practical importance and theoretical interest. No researches specifically devoted to this subject have appeared, but incidentally a number of new circumstances in which it arises have been observed by Lüppo-Cramer.[46] The frequently expressed opinion that chemical fog is due to partial or to excessive chemical reduction of the silver halide by reducing products, formed during the hydrolysis of gelatin which occurs during ripening, may be, and probably is, one possible cause but certainly does not cover more than a small proportion of all cases. For instance, the large granules or small clots of a badly-made (granular) emulsion are always rapidly reduced in development, even in a slow almost unripened emulsion, while the writer has experience of a bromochloride emulsion (boiling method) which was prone to black fog when ripened by standing for 5 minutes in boiling water, but which gave no fog if the boiling treatment was increased to 8 or 9 minutes. There seems to be much to support the idea that electrically neutral particles of silver halide are instantly reducible by a photographic developer whether embedded in a colloid vehicle or not. There are so many known ways of inducing chemical fog that it is now highly desirable to submit them to a thorough study in the hope that their ultimate causes may be reduced to a few and based on fundamental principles.

Photomechanical Processes.

In this direction no striking new development appears to have taken place apart from the "Photosculpture" process due to H. M. Edmunds already referred to, which, properly speaking, falls under this heading.

The year has been chiefly notable for the many attempts that have been made by lithographic firms to apply the three-colour process to lithography. The chief difficulty encountered has been the necessary retouching, which cannot be so readily carried out on lithographic zinc plates as it can on half-tone blocks. One method of overcoming this difficulty has been provisionally protected by A. E. Bawtree. It consists of applying to each patch of colour in the original a piece of suitably-coloured cellophane; this alters the colours of the original by an amount which corrects the change in reproduction, so that the colours as reproduced should be correct.

The old idea of impressing a grain, regular or irregular, upon a collotype plate instead of using the natural reticulation of the film, has been revived by A. R. Trist, who is using for this purpose a regular screen with fine lines. So far as this work has gone, it indicates that there is a possibility of obtaining collotype plates

[46] Lüppo-Cramer, *Die Phot.*, 1921, No. 3, 1.

that are easily inked, and will give longer runs in the printing machines.

A recent paper by H. M. Cartwright[47] on the rendering of tone values by rotary photogravure is a welcome indication that modern methods of dealing with tone reproduction problems are being applied to photomechanical processes. Such studies will surely lead to improvements in technique based on accurate knowledge in a field where, hitherto, empiricism has reigned supreme.

Radiography.

The formation[48] of The Society of Radiographers, designed to include all qualified non-medical assistants who are engaged in the practical application of X-rays under the direction of Medical Officers, is a noteworthy step. It is to be expected that one useful result of this new departure will be an all-round improvement in the conditions under which such assistants have to work and a higher percentage of first-class skiagrams.

In some X-ray departments, even in quite important institutions, there has been only a very scanty appreciation of the importance of a thorough acquaintance with photographic technique, and the advantages of well-equipped darkrooms.

An interesting novelty in X-ray-sensitive materials due to L. A. Levy, A. L. Landau, and T. T. Baker[49] has been put on the market. It consists of a silver gelatino-bromide plate having a hardened emulsion film upon which is coated another and a readily-soluble gelatin layer carrying fluorescent calcium tungstate. After exposure, stated to range from one-fifth to one thirty-fifth of that required for ordinary X-ray plates according to the hardness of the radiation employed, the upper film is washed away in hot water and the lower film of hardened emulsion is developed. Any such method, involving the coating and subsequent removal of a fluorescent layer in intimate contact with the sensitive emulsion, necessarily has drawbacks and it is to be hoped that some water-soluble highly-fluorescent substance which can be incorporated harmlessly with the emulsion will ultimately be found, though a large amount of investigation has, so far, failed to disclose one which is both highly active and not injurious either to the sensitiveness or the stability of the silver halides.

It has been found unsafe to produce X-ray motion pictures by photographing a fluorescent screen image with the aid of a kinema camera,[50] the radiation necessary being so intense as to endanger the patient.

[47] H. M. Cartwright, *Phot. J.*, 1921, **61**, 428.

[48] *J. Rönt. Soc.*, 1921, **17**, 22.

[49] L. A. Levy and A. L. Landau, E.P. 163,903. L. Levy, D. W. West, T. T. Baker, *J. Ront. Soc.*, 1921, **17**, 55, 104; *Phot. J.*, 1921, **61**, 158.

[50] *Eastman Kodak Res. Lab. Report No.* 1130.

A valuable contribution to the technique of radiography is a paper by R. B. Wilsey[51] on the intensity of scattered X-rays in radiography, in which he shows what a small proportion of the total radiation reaching the plate consists of useful image-forming rays when thick subjects are being radiographed or large diaphragms used.

The same investigator[52] has employed homogeneous X-rays to determine the structure of the crystal lattice in precipitated flocculent silver chloride, bromide, and iodide, and shows that these apparently amorphous precipitates are definitely crystalline in their ultimate structure and belong to the cubic system. He proposes to proceed to the examination of the crystalline grains of photographic emulsions by similar methods. The results will be awaited with great interest since such studies will probably throw light on the question of the distribution of the iodine atoms in the crystals of a silver iodobromide emulsion. There has been a strong inclination to assume, without any sort of proof, that such crystals are homogeneous solid solutions of the two halides, but some observations of the writer's on the coprecipitation of these salts seem to make this supposition doubtful (see later).

Photographic Emulsions.

Experimental work on emulsion making is but rarely published. The past year is exceptional in that a few such papers have appeared giving the conclusions which have been drawn from the results, but in each case important experimental details are purposely omitted. P. Knoche[53] has unsuccessfully sought to gain some advantage by delaying the formation of the silver halide by substituting brominated organic compounds for the usual alkali bromides. C. A. Schleussner and H. Beck[54] publish the results of an attempt to elucidate the effect of varying the proportion of iodide in silver iodobromide emulsions. They find an optimum steepness of gradation and sensitiveness for a certain iodide percentage (which, however, changes with the conditions under which the emulsion is mixed) and a maximum X-ray sensitiveness in pure bromide emulsions; other points are also discussed. Their division of such emulsions into three classes is useful, but the assumption that emulsions formed by the addition of silver solutions to the mixed halides leads to the formation of a double compound of AgBr and AgI during the emulsification, and that this method therefore guarantees uniformity of composition of the precipitated grains, is in the writer's opinion not justifiable. It is easy to show

[51] R. B. Wilsey, *Amer. J. Roent.*, 1921, **8**, 328.
[52] R. B. Wilsey, *Phil. Mag.*, 1921, **42**, 262.
[53] P. Knoche, *Phot. Rund.*, 1921, **57**, 49.
[54] C. A. Schleussner and H. Beck, *Z. wiss. Phot.*, 1921, **21**, 105.

that (in the presence of ammonia) the silver iodide (or a more insoluble iodide-bromide complex) is always precipitated before the bulk of the bromide, and there is apparently no reason therefore why the iodide should be uniformly distributed in any crystal or why different grains should not vary considerably in the proportions of silver bromide to iodide composing them in the early stages of ripening and very possibly even in the finished emulsion.

W. T. Wilkinson[55] has recently advocated the use of a mixture of bromide and chloride instead of the usual iodising solution in the wet collodion process, which still occupies a strong position in line and half-tone work.

There have been several important papers and discussions concerning the relation between sensitiveness and grain size of silver halide emulsions. Mees[56] has abandoned his earlier assumption of a direct connexion between grain size and sensitiveness, a conclusion shown to be inevitable by the work of Svedberg (mentioned in last year's report, since published in English[57] with interesting extensions to the action of α- and β-particles) and confirmed in some emulsion-making experiments by the writer[58] and by A. P. H. Trivelli and S. E. Sheppard.[59] Svedberg's work has been recently extended by F. C. Toy,[60] who showed that even grains of identical area, shape, and thickness may vary greatly in sensitivity. J. Brooksbank[61] has shown that in the rate and degree of visible darkening of the grains in light there is a similar want of relation to size and shape. We are therefore compelled to assume differences in the molecular construction and/or the chemical composition of the crystals to be the prime factors determining the sensitivity of the individual grains, though it must still be admitted that to attain a given sensitiveness it seems from practical experience necessary that a certain minimum average size of grain should be exceeded.

Practically nothing is known at present except in a purely empirical fashion about the effects of the conditions of precipitation on the grain size of silver halide emulsions. A few experiments bearing on the subject are to be found in Trivelli and Sheppard's monograph already mentioned, but inasmuch as the results have a considerable commercial value it is unlikely that any detailed studies will be published by those engaged in the industry.

55 Royal Photographic Society Meeting, Nov. 8, 1921.

56 C. E. K. Mees, *J. Franklin Inst.*, 1921, **191**, 631.

57 T. Svedberg and H. Andersson, *Phot. J.*, 1921, **61**, 325; *J.*, 1921, 638A.

58 F. F. Renwick, *Phot. J.*, 1921, **61**, 333; *J.*, 1921, 638A.

59 Monograph, "The Silver Bromide Grain of Photographic Emulsions," by A. P. H. Trivelli and S. E. Sheppard, p. 104. S. E. Sheppard and A. P. H. Trivelli, *Phot. J.*, 1921, **61**, 400.

60 F. C. Toy, *Phot. J.*, 1921, **61**, 417.

61 J. Brooksbank, *Phot. J.*, 1921, **61**, 421.

Recent papers by von Weimarn, S. Odén, and others,[62] are, however, sufficient to show the extreme difficulty of such researches even in such relatively simple cases as barium sulphate precipitates. Svedberg's recently published little book on "The Formation of Colloids" contains a brief account of some of their results and a valuable bibliography. The fullest development of the art of emulsion making is likely to depend on the results of such studies, and therefore men of the highest scientific qualifications will undoubtedly be required in the industry in considerable numbers, and will need very well-equipped laboratories.

An interesting mathematical study by L. Silberstein[63] demonstrates how, as a consequence of the drying of the gelatin film, the great majority of the silver bromide grains in a dry plate lie approximately parallel to the surface.

Reactions of Photographic Images.

A. Steigmann[64] during the past two years has investigated the applicability of the hydrosulphites to various photographic purposes (developing, silver recovery, etc.) but finds them of no great value in most cases, though convenient for recovering the silver from old fixing baths and incidentally regenerating them.

The process of photographic reduction by means of persulphates has received a large amount of attention. Lumière and Seyewetz[65] reaffirm their view that the selective action of these reagents on the denser parts of the developed image is due to the tendency to reversal of the initial solvent action when the silver sulphate first formed is in presence of excess of persulphate, photographic reduction (silver removal) being thereby confined to the deeper layers of the film. They do not accept Sheppard's view that the irregularities met with are attributable to variations in iron content and state, that for regular action a definite free acid content of $\frac{1}{4}$–$\frac{1}{2}$% is alone necessary unless chlorides, which are particularly potent in modifying the action, are present. A valuable historical summary of previous work on persulphate reduction has been published by G. I. Higson, with a very full bibliography.[66] Lastly, a valuable series of new experiments on the subject and a detailed

[62] S. Odén, *Arkiv för Kemi*, 1920, **7**, No. 26, 1-03. For other papers on size of particles *see* S. Odén, *Proc. Roy. Soc. Edin.*, 1915-16, **36**, 220; *Bull. Geol. Inst., Upsala*, **16**, 15, 125; and other papers. Also H. Green, *J. Franklin Inst.*, 1921, **192**, 637.

[63] L. Silberstein, *J. Opt. Soc. Amer.*, 1921, **5**, 171, 363; *J.*, 1921, 340A, 791A.

[64] A. Steigmann, *Kolloid-Zeits.*, 1920, **27**, 249; **28**, 29, 175; *J.*, 1921, 164A, 325A. *Phot. Ind.*, 1921, 379.

[65] A. and L. Lumière and A. Seyewetz, *Brit. J. Phot.*, 1921, **68**, 124.

[66] G. I. Higson, *Phot. J.*, 1921, **61**, 237.

discussion of their probable explanation which has just appeared in a paper by S. E. Sheppard,[67] confirms Lumière and Seyewetz' observations on the importance of the acidity of the solution, and sets the whole matter in a somewhat clearer light.

A useful paper by L. A. Jones and C. E. Fawkes[68] deals quantitatively with the effects of ten different photographic reducing agents upon developed images on paper.

The high degree of permanence attaching to sulphide-toned silver images and the beauty of some of the brown tones so obtained has attracted several workers to the study of sulphide toning processes and, as a natural extension, to the working out of methods of toning with selenium and tellurium.

Lumière[69] claims the use of thiophosphates as sulphiding agents, having the merit of being odourless. The theory of sulphide toning in the hypo-alum bath is partly elucidated in a paper by H. Freundlich and A. Nathansohn,[70] and in a recent paper before the Royal Photographic Society by S. O. Rawling,[71] not yet published, the former showing that colloidal sulphur is able to combine directly with colloidal silver, and the latter that at a moderately elevated temperature the same reaction can take place with the silver of a developed print.

A detailed study of the effects of varying the compositions of the bleaching and sulphiding baths and other details of manipulation has been published by E. R. Bullock.[72]

Namias[73] has published several new formulæ for toning with selenium and a number of patents for selenium and tellurium toning baths have been taken out by German firms.[74] H. Franke[75] has patented a process of intensification by means of selenium.

A new printing process has been patented by the Badische Anilin u. Soda Fabrik.[76] When benzidine or other diamine compound is precipitated with an acid dye (*e.g.*, Eosin, Cyananthrol, Neptune Green, or Quinoline Yellow S) an insoluble compound is formed which in the presence of manganese nitrate or other suitable

[67] S. E. Sheppard, *Phot. J.*, 1921, **61**, 450.

[68] L. A. Jones and C. E. Fawkes, *J. Franklin Inst.*, 1921, **191**, 503; *J.*, 1921, 370A.

[69] A. Lumière, F.P. 507,332.

[70] H. Freundlich and A. Nathansohn, *Kolloid-Zeits.*, 1921, **28**, 16.

[71] S. O. Rawling, Royal Photographic Society Meeting, Nov. 8, 1921.

[72] E. R. Bullock, *Brit. J. Phot.*, 1921, 447; *J.*, 1921, 639A.

[73] R. Namias, *Il Prog. Fot.*, 1921, **28**, 14.

[74] Chem. Fabr. auf Aktien (vorm. E. Schering), G.P. 335,627; *J.*, 1921, 562A. Kraft und Steudel, G.P. 334,172 and 337,820; *J.*, 1921, 413A, 639A. Mimosa A.-G., G.P. 337,869; *J.*, 1921, 639A. E.P. 169,378.

[75] H. Franke, G.P. 333,094; *J.*, 1921, 371A.

[76] Badische Anilin u. Soda Fabrik, G.P. 337,173; *J.*, 1921, 639A. See also J. M. Eder, *Brit. J. Phot.*, 1921, **68**, 658.

oxidising agent bleaches in the light. According to the base and the acid dye selected, prints of a large variety of colours are obtainable having good gradation and vigour. "Fixing" is done in borax or sodium phosphate. Pure whites have not yet been obtained and printing is very slow, but the process appears to be worth further study.

Miscellaneous.

An interesting paper by J. Rheinberg[77] draws attention to the change in permeability to alcohol of certain colloid films containing ferric ammonium citrate after this salt has been reduced by exposure to light. This phenomenon is the basis of his patents relating to a multicolour screen suitable for colour photography (*vide* J., 1913, 1116; 1914, 513, 637). It is to be expected that a variety of useful applications could be found for this remarkable property of such exposed films.

A new type of electric lamp, "Osglim," is being put on the market by the General Electric Co., having interesting possibilities for dark-room illumination. The light emitted arises from an electric discharge between electrodes in a bulb filled with neon, or neon and mercury vapour. Although the candle-power per watt is very low, recent experiments in the laboratories of Ilford, Ltd. have shown that with suitable safelight screens they are more efficient for darkroom illumination than ordinary metal filament lamps, besides having a long life and generating very little heat, the consumption being only 5 watts per lamp.

Theory.

A number of papers of a mathematical nature dealing with the various characteristics of silver bromide emulsions has appeared. In view of the number and complexity of the factors involved, it is unlikely that a mathematical solution embracing all such emulsions will prove possible, so that while a thorough study of all these factors and their inter-relations is highly desirable and is indirectly valuable both to the manufacturer and to those who use dry plates for quantitative work, it would not repay users to determine the 'constants' in the very complex equations suggested for the characteristic curve by Ross, Helmick, or Slade and Higson.[78]

The Hurter and Driffield method of determining the "inertia" of a plate is well known to give results of an unreliable character

[77] J. Rheinberg, *Phot. J.*, 1921, **61**, 120; *J.*, 1921, 239A, 603A.

[78] F. E. Ross, *Astrophys. J.*, 1920, 201; *J. Brit. Astr. Assoc.*, 1920, **31**, 25; *J. Opt. Soc. Amer.*, 1920, **4**, 255; *J.*, 1921, 323A. P. S. Helmick, *Phys. Rev.*, 1921, **17**, 135; *J.*, 1921, 239A. R. E. Slade and G. I. Higson, *Proc. Roy. Soc.*, 1920, A **98**, 154; *J.*, 1921, 27A.

if used alone as a criterion of sensitiveness, because of the considerable variations among commercial plates in the relative lengths of the lower and the middle, approximately straight, parts of the characteristic curve and the uncertainties arising from variations in the amount of chemical fog in different plates and for different times of development. Moreover, in all photometric work in which light intensities are to be deduced from their effects on photographic emulsions, the greatest care has to be exercised to avoid numerous possible sources of error even when adopting the apparently simple method of comparing the unknown with a series of known values recorded on the same plate or film, so that to rely on values deduced from a formula would be practically useless.

In two important papers G. I. Higson[79] makes an ambitious attempt to reconstruct the Hurter and Driffield characteristic curve by reasoning based on Slade and Higson's paper on the photochemical law of the silver halide grain published last year. While the mathematical reasoning in these papers has met with severe criticism[80] and is based on assumptions difficult in some cases to justify, it is important to note that Slade and Higson's experimental work, showing that "under ordinary conditions of exposure (for times over about $\frac{1}{100}$-sec. and with white light) and with most plates on the market, the density is proportional to the square of the exposure in the under-exposure region" has been confirmed by F. C. Toy.[27]

The experimental section of Higson's second paper merits careful attention from all workers in sensitometry, and lends considerable support to the mathematical introduction.

Methods of sensitometry, based on the properties of neutral optical wedges, are rapidly coming into general use, both in this country and on the Continent. In connexion with them a paper by G. I. Higson is a useful addition to the literature of the subject.[81]

A new and rapid method of determining absolute reflection coefficients as the result of two observations only has been worked out by A. H. Taylor[82] and independently by C. H. Sharp and W. F. Little,[83] while the former has devised for the purpose a very ingenious portable instrument which should prove a valuable addition to the equipment of any laboratory concerned with the photometry of paper or other reflecting surfaces, prints, etc.

[79] G. I. Higson, *Phot. J.*, 1921, **61**, 35, 144; *J.*, 1921, 99A, 239A.

[80] L. Silberstein and S. E. Sheppard, *Phot. J.*, 1921, **61**, 205, 206, 252; *J.*, 1921, 324A.

[81] G. I. Higson, *Phot. J.*, 1921, **61**, 93; *J.*, 1921, 163A.

[82] A. H. Taylor, *Bull. Bur. Stand.*, 1920, **16**, 421, and *Scient. Paper No.* 391; *Bull. Bur. Stand.*, 1920, **17**, 1; *Scient. Paper No.* 405.

[83] C. H. Sharp and W. F. Little, *Trans. Ill. Eng. Soc. Amer.*, 1920, 802,

Several suggestions to employ self-luminous mixtures of radioactive and fluorescent substances as a rough standard of light have been made: (a) for the preparation of sensitometric tablets,[84] (b) as the comparison source in an actinometer.[85]

PHOTOCHEMISTRY OF SILVER SALTS.

Two papers have appeared dealing quantitatively with the photochemical decomposition of silver bromide in strong illumination. In the first, by W. Ehlers and P. P. Koch,[86] finely-divided dry silver bromide particles were "weighed" in an Ehrenhaft-Millikan condenser and found to show a slight gain in an oxygen-containing atmosphere and a loss (reaching 10% for the smallest particles) in an atmosphere of nitrogen when exposed to a strong light. It is deduced from calculations based on these results, *obtained under very different conditions*, that in the photochemical decomposition of highly sensitive silver bromide by weak light a loss of weight occurs corresponding to approximately 1 Br atom per particle of AgBr. The second paper, by R. Schwarz and H. Stock,[87] deals with the rate of elimination of bromine from wet precipitated silver bromide when exposed to daylight in three different states of aggregation, obtained by adding excess of a potassium bromide solution to an acid silver nitrate solution, and from a fourth variety obtained when excess of silver nitrate was employed. Considerable variations in sensitiveness were observed between the different specimens. The curves connecting the average rates of loss of bromine per hour with the logarithms of the average light intensities during exposure are said to be similar in type to the characteristic curves of photographic emulsions. Beyond a certain average intensity of illumination a sharp fall in the average rate of loss of bromine was observed, and consequently it is asserted that solarisation is accompanied by a diminution in the rate of its elimination. In view, however, of the difficulties invariably found in making a number of separate preparations of similar sensitiveness on a small scale, the results are of doubtful trustworthiness while, in any case, the above curves do not show the course of the reaction during its progress for any given preparation and for a given light intensity as does the characteristic curve of a plate.

Further studies of the effects of coloured lights on the photochlorides of silver by F. Weigert[88] emphasise once again the marshal-

[84] E. Huse, *Eastman Kodak Res. Lab. Rep. No.* 1102.

[85] C. C. Howenstine, U.S.P. 1,361,999. F. J. Hargreaves, F.P. 519,081.

[86] W. Ehlers and P. P. Koch, *Z. f. Physik*, 1920, **169**; *J.C.S. Abst.*, 1921, **120**, 289.

[87] R. Schwarz and H. Stock, *Ber.*, 1921, **54**, 2111; *J.*, 1920, 791A.

[88] F. Weigert, *Ann. d. Physik*, 1920, **63**, 681; *Kolloid-Zeits.*, 1921, **28**, 115, 153.

ling action or regimentation which light waves exert on ultramicroscopic particles, while a new method of preparing silver sols having particles of known dimensions which has been worked out by K. Schaum and H. Lang[89] is a valuable contribution to the question of the relations between colour and size of particle in such complexes, a subject which is discussed by F. Formstecher[90] in its bearings on chlorocitrate print-out processes.

It is being urged by some prominent scientific workers that all chemical reactions and changes of state are initiated by radiation.[91] Confining ourselves to generally acknowledged photochemical changes, however, it certainly seems necessary in all cases to assume that the absorption of light energy leads to a liberation of latent valencies (electrons), or some activation of the molecule, as the initial step in the process, the succeeding stages depending chiefly on the nature of the neighbouring molecules.[92]

The writer's suggested modification of the silver germ theory of the latent photographic image has been criticised by Lüppo-Cramer[93] and S. E. Sheppard,[94] who are both of the opinion that the suggested photoelectric discharge of negative electrons from colloidal silver held in solid solution in silver bromide (resulting in electrically neutral silver gel particles) is improbable. In this connexion it is of interest to note H. P. Stevens' observations[95] on the rapid (and reversible) change of certain rubber sols into gels on exposure to light, while to the writer it seems inconsistent of Lüppo-Cramer[96] to attribute the fogging action of certain basic dyes and neutral salts to the neutralisation of the negative electric charges on the silver amicrons supposed to be formed in the ripening process and yet to deny the possibility of light bringing about the developable condition by the removal of these electric charges.

M. Volmer[97] assumes that by the action of light a change in the silver bromide grains arises at individual points, resulting in differently attached silver atoms, while Sheppard and Trivelli[59] suggest that "some degree of migration and oriented concentration of the silver cations will occur in the silver halide crystal lattice which will favour the essential photochemical change, *i.e.*,

[89] K. Schaum and H. Lang, *Kolloid-Zeits.*, 1921, **28**, 243; *J.*, 1921, 561A.

[90] F. Formstecher, *Phot. Ind.*, 1921, 439, 455, 590.

[91] Faraday Society, Discussion on Chemical Change and Catalysis, Sept. 28, 1921; *J.*, 1921, 367R. See also Brit. Assoc. Address, Prof. O. W. Richardson, *Nature*, 1921, Nov. 17, 372.

[92] P. R. Kögel, *Phot. Korr.*, 1920, **57**, 308; 1921, **58**, 65.

[93] Lüppo-Cramer, *Phot. Korr.*, 1920, **57**, 259, 285.

[94] S. E. Sheppard, *Brit. J. Phot.*, 1921, **68**, 4.

[95] H. P. Stevens, *J.*, 1921, 187T.

[96] Lüppo-Cramer, *Die Phot.*, 1921, No. 9; see also "Kolloidchemie u. Photographie," 2nd ed., p. 108.

[97] M. Volmer, *Z. wiss. Phot.*, 1921, **20**, 189; *J.*, 1921, 239A.

$Br'.Ag^{\cdot} \longrightarrow Br + Ag$; in words, the passage of an electron from a bromine ion of the lattice to a silver ion"; they promise to discuss the energy relations later. The crux of the problem lies in the deficiency of energy for the effects produced, and in this respect it is on all fours with the difficulties discussed by Prof. O. W. Richardson[91] in his recent Presidential Address to the British Association.

Theory of Development.

In March, 1920, the writer[98] called attention to the catalytic nature of the process of chemical development and pointed out the possibility that the effect of a reagent which apparently "destroyed" the latent image might in some cases be due to "poisoning" of the catalyst formed by light instead of its removal by solution or transformation into a new chemical compound.

The catalytic character of the development process forms the theme of the paper by M. Volmer[97] cited above. He emphasises the difficulty of accepting the older idea underlying the silver germ theory of the latent image, according to which there was no essential difference between chemical and physical development except in the origin of the deposited silver, the original nucleus in either case growing by accretion as the silver gets thrown out from a supersaturated solution.

On the catalysis theory of chemical development, however, the silver bromide grains are rapidly reduced *in situ* as a result of contact catalysis, the processes of solution, reduction to silver, and its deposition being accomplished without bringing into play the transportation of supersaturated silver solutions outside the ambit of the individual grain. A paper by A. Steigmann[99] also clearly brings out the distinctions between the two modes of developing a latent image.

Sheppard and Meyer[100] have previously advanced the opinion that reduction of the silver bromide grain is preceded by adsorption of the reducing agent and takes place in the breakdown of this adsorption complex, the process being accelerated or initiated by the latent image as silver nucleus. In the paper already cited this is amplified.

In the light of the accelerating effects already referred to (of phenosafranine on quinol developers and the mere dilution of some other developers) it is clear that differences in the initial rate of attack, on which the old arbitrary distinction between "slow" and "rapid" developers was chiefly based, are a very uncertain index of the relative energies of different agents. While we must

[98] F. F. Renwick, *J.*, 1920, 156T.

[99] A. Steigmann, *Phot. Ind.*, 1921, 55

[100] S. E. Sheppard and G. Meyer, *Phot. J.*, 1920, **60**, 12.

The heats of combustion of numerous aromatic compounds, determined in the Research Department by W. E. Garner and C. L. Abernethy, have now been published.[32] These differ materially from the heats of detonation because oxidation is complete. From the heats of combustion the heats of formation from the elements are calculated.

Sensitiveness.

The determination of this property with accuracy is attended with great difficulties, as it is affected by the nature of the surfaces between which it is tested and the physical condition of the explosive itself. The falling weight apparatus is the only one which gives results which can be expressed readily in figures, but here the further difficulty comes in of deciding whether in any experiment the explosive has exploded. This has been overcome by an ingenious device of Rotter's, whereby the small quantity of explosive under test is in an air-tight space and the quantity of gas evolved can therefore be measured. The degree of insensitiveness is measured by the blow that is required to decompose half of the explosive. To avoid the uncertainty due to the surfaces they are standardised each time by testing a standard explosive, such as gunpowder, picric acid, or fulminate. The following are some of the "figures of insensitiveness":—Mercury fulminate, 10; nitroglycerin, 13; dry guncotton, 23; tetryl, 70; tetranitroaniline, 86; picric acid (standard), 100; trinitrotoluene, 115; amatol, 80/20, 120.

Falling weight determinations have also been carried out by C. F. van Duin and B. C. R. van Lennep[33] on a considerable number of specially prepared nitro-compounds to ascertain the effects of constitution and substitutions on the sensitiveness. They find that compounds containing two nitro-groups in the *ortho*-position to one another are always somewhat sensitive in consequence of the mobility of the nitro-group. Consequently tetranitrobenzene derivatives are always much more sensitive than trinitro, but the presence of amino-groups increases the stability, whereas a methylnitroamino-group renders it more sensitive. Thus tetranitroaniline is slightly less sensitive than trinitrophenylmethylnitroamino and tetranitro-*m*-phenylenediamine is much more insensitive.

Power is a function of the heat of detonation and the volume of gas evolved. The French calculate the "force" from the volume of the gases at the temperature of explosion, but the latter can only be arrived at by making assumptions as to the specific heats of the gases, and there is great uncertainty as to these at the high temperatures involved. It is measured directly either by the ballistic pendulum or the Trauzl lead block test, more usually the

[32] *Proc. Roy. Soc.*, 1921, A 99, 213; *J.*, 1921, 530A.
[33] *Rec. Trav. Chim.*, 1920, [illegible]5; *J.*, 1920, 67[illegible]

Br'.Ag though here again there is a difficulty in obtaining consistent bromine results. The test has been re-examined by H. Kast, who confirms that the volume of the enlargement is practically independent of the density of the explosive, but the lead should be standardised by firing a standard explosive in it, and the results should be corrected for the temperature of the experiment, as follows: −10° C., correction +10%; 0° C., correction +5%; +5° C. correction +3·5%; +10° C., correction +2·0%; +15° C., correction 0%; +20° C., correction −2%.

Violence.

Another factor which greatly influences the effects produced by explosives both for military and civil purposes is the rate of detonation. The violence can be measured directly by the crushing effect on small copper cylinders, a method which has been developed by H. Kast,[34] who gives a number of determinations made by this and other tests. The cartridge of explosive is unconfined and should be not less than 7 cm. long. The amount of crushing of the copper is then independent of the length of the cartridge and is approximately proportional to the product of the power of the explosive, its density and its velocity of detonation. He gives the following results :—

Explosive.	Density (Δ)	Vely. of detn. m/sec. (V).	Trauzl c.c. (P).	$\frac{\Delta VP}{10^6}$	Crushing test.
Blasting gelatin	1·63	7800	490	6·2	4·8
Nitroglycerin	1·60	7450	485	5·9	4·6
Tetryl	1·63	7200	330	3·9	4·2
Hexanitrodiphenylamine	1·64	7100	300	3·5	4·1
Trinitrobenzene	1·63	7000	310	3·5	4·1
Picric acid	1·69	7100	290	3·5	4·1
Trinitrochlorobenzene	1·74	7100	290	3·6	4·1
Gelignite	1·66	6100	365	3·7	3·9
Trinitroanisole	1·59	6660	285	3·0	3·6
Trinitrotoluene	1·59	6700	280	3·0	3·6
Trinitrocresol	1·62	6850	270	3·0	3·5
Dynamite No. 1	1·50	6650	300	3·0	3·1
Guncotton (dry)	1·30	6300	340	2·8	3·0
Amatol 40/60	1·56	5330	330	[illegible]	2·9
Dinitrobenzene	1·50	6100	245	2·2	2·9
T ammonal	1·60	5400	410	3·6	2·8
Guncotton (wet)	1·28	6800	275	2·4	2·7
Cheddite B	1·3	4000	400	2·1	2·3
Donarit	1·3	4000	360	1·9	2·0
Cheddite 60	1·3	3000	250	1·0	1·4

In considering these results it should be borne in mind that blasting gelatin, nitroglycerin, and ammonal probably give abnormally high results in the Trauzl test because the lead is unduly [illegible] the very hot gases evolved, and some of the more insen-

[illegible] A. [illegible]

[100] S. E. Sheppard, [illegible] 14, [illegible] 1, 181; J., 1920, 705A.

admit the formation of more easily reducible adsorption complexes in the cases above mentioned, and in many other similar phenomena, some unpublished experiments of the writer's show that exposed plates bathed for 1 minute in 1 : 1000 neutral solutions of Chrysoidine or Patent Blue are developable only with extreme slowness in most developers, thus demonstrating the possibility of "poisoning" the catalytic activity of the latent image by the formation of an adsorption complex with the silver halide of quite the opposite character. In these cases also the effect varies in degree with the reducing agent employed and is sufficiently powerful with quinol and some substituted quinols to make development practically impossible. Removal of the dye by prolonged soaking in suitable baths (weak acetic acid for Chrysoidine and weak alkali for Patent Blue) restores the capacity for development.

That the catalytic activity of the latent image may be poisoned similarly by mercuric chloride is suggested by A. St. H.[101] to account for the "destructive" action of this salt when intensification of the latent image might have been expected.

In connexion with catalytic reactions of this kind, it would be well worth while to investigate in a scientific and quantitative manner the well-known catalytic accelerating actions of traces of lead, bismuth, and mercury salts in the development of cold-bath platinotype paper, while the extraordinarily powerful poisoning action of tartar emetic on this development reaction (writer's observation, not previously published) is of considerable interest.

E. C. C. Baly and his co-workers[102] have published two important photochemical papers during the year, the first dealing with the mechanism of the combination of hydrogen and chlorine on illumination, and the second with the photo-synthesis of formaldehyde and carbohydrates from carbon dioxide and water. In the former paper strong arguments are adduced in favour of the view that the cause of the considerable deviation from a simple proportional relationship between the reaction velocity and the light intensity is due to the re-absorption by the reactant molecules (uncombined chlorine and hydrogen) of the energy radiated by the hydrogen chloride in process of formation, with the result that many more of the former become activated than would otherwise be the case. In this, and more fully in the second of the above mentioned papers, a new hypothesis to account for photocatalysis (colour-sensitising) of a photochemical reaction is suggested. According to Baly a photocatalyst must contain the same elementary atoms as the light-sensitive substance or must form a compound or complex with it, but although he states that the sensitisation of photographic

[101] A. St. H., *Phot. Ind.*, 1921, 296.

[102] E. C. C. Baly and W. F. Barker, *Chem. Soc. Trans.*, 1921, **119**, 653. E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *ibid.*, 1921, **119**, 1025.

plates to red and yellow light can probably be explained on these lines he does not discuss the subject further. At present we have no real foundation on which to build up a theory of colour-sensitising for we do not know what factors are indispensable. Most workers believe that there must be some sort of union or adsorption between the dye and the silver halide, but it is evident that it may be a very loose connexion since the considerable blue-sensitiveness conferred on silver chloride by Auramine is readily removed by washing out the dye with water only. Baly's views on this subject are far too general in character to be of any assistance to photographic chemists at present in the search for efficient sensitisers.

It has now become almost impossible for any one worker in photographic science to appreciate at their truo value, or even to follow closely, the advances being continually made in the many fields of inquiry from which photography daily draws fresh inspiration, but if this report achieves its purpose, even in a minor degree, it cannot fail to indicate something of the diversity, difficulty, and fascination of the subject.

EXPLOSIVES.

By A. Marshall,

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American Explosives Law.[1]

Before the United States entered the war in 1917 the regulation of explosives was in the hands of tho individual states except as regards inter-state commerce. The prevalence of bomb outrages by enemy agents and others then made it necessary to pass a uniform law for the whole country, and exercise far greater control. An Act was therefore adopted and approved on October 6, 1917, and, like much war-time legislation, it was of a very drastic character, for it not only rendered it necessary to obtain a licence "to have in possession or purchase, accept, receive, sell, give, barter or otherwise dispose of or procure explosives," but the same restrictions were extended to ingredients except when purchased or held in small quantities and not used or intended to be used in the manufacture of explosives. As practically any substance under the sun could be usod as an ingredient of an explosive it was necessary in the administration of the Act to restrict this part of it to oxygen carriers. Even so a licence had to be issued not only to every druggist and doctor, but also to every butcher who required saltpetre to salt his meat and to the members of many other professions and trades.

Numerous licensing agents were appointed under the Act, and their inquiries revealed a most deplorable state of affairs. Great stores of explosives were found within the limits of cities and towns. In hundreds of places explosives had been abandoned by the owners without any protection whatsoever. Thousands of storage places were of such poor construction that any person could enter and obtain explosives for criminal purposes, and this had been the usual practice of "safe blowers" and other criminals, in spite of the fact that dynamite could be bought as easily as cheese.

Notwithstanding the great improvements effected by the enforcement of this Act, it was naturally unpopular on account of the interference with so many ordinary and innocent occupations,

[1] See *Bull.* 198 *of U.S. Bureau of Mines*, by C. E. Munroe, 1921.

so although the Act remains in force until the United States are declared officially to be no longer at war, shortly after the armistice the activities of the inspectors were greatly reduced by cutting off supplies of money. Licences were done away with for vendors, purchasers, foremen, analysts, educators, investors, and investigators, and are now required only for manufacturers, exporters, and importers. It is proposed, therefore, that a new law be enacted for the regulation of the manufacture, storage, sale and use of explosives.

Gunpowder.

Saltpetre.

Gunpowder is still used for many purposes in the manufacture of munition, such as filling the time rings of fuzes, pellets, and ignition charges, safety fuze and the opening charges of shrapnel shell, and consequently there was a greatly increased demand for potassium nitrate just at the time when the principal supply of potash salts, the Stassfurt mines, was cut off from the Allies. Other sources were therefore developed, and especially the Indian saltpetre industry. The output in Bihar, which was formerly the principal seat of the industry, did not increase very much, but in the United Provinces and the Punjab the production rose so much that in both these provinces it was larger than in Bihar. The methods of the Indian saltpetre workers have been investigated both bacteriologically and chemically by C. M. Hutchinson, who finds that they are not irrational, although they might be improved in some respects, especially if the Indian Salt Department did not interfere so much.[2]

Attempts were also made to develop supplies from Chile[3] and South Africa,[4] but these had not amounted to much when the war ceased.

For ordinary blasting purposes the difficulty was overcome by using sodium nitrate instead of the potassium salt, and the sanction for this substitution is to be permanent in the United Kingdom.[5] In many factories structural alterations were necessary in consequence of the hygroscopic character of sodium nitrate. As this salt is considerably cheaper than saltpetre its use should check the diminution in the consumption of black blasting powder. In America, where it has always been used, the output does not tend to decrease. The milling and other processes of manufacture can also be shortened and cheapened.

[2] *Bull.* 68, *Agric. Res. Inst., Pusa.*

[3] *J.*, 1920, 221R.

[4] E. G. Bryant, *J.*, 1921, 360T, 435R.

[5] *Ann. Rept. of H.M. Inspector of Explosives*, 1914, 3.

NITROCELLULOSE.

Cotton.

Until recently practically the only variety of cotton used for the manufacture of guncotton for cordite and other service explosives in England was cotton waste, and before the war the waste that was supplied to the makers of the guncotton was generally of poor quality in spite of the rigid specification that it had to pass. The good "spun" waste was broken down and re-spun for the manufacture of cotton blankets, etc., and much of it was exported to Germany and Belgium for this purpose. The material used for the manufacture of guncotton was therefore the sweepings of the cotton mills, which had to be submitted to a drastic purification process, causing a partial breaking down of the cellulose complex. During the war the average quality of the cotton waste used appears to have been better, but at present, of course, the high-class waste is again being worked up into textile materials. The British Navy has now abandoned the use of cotton waste and has adopted instead "sliver," which is the purified fibre in the form of loose strips before it has been spun.[6] This must give a more stable nitrocotton. It is possible that the Army will adopt the same material. Sliver when examined under the microscope by W. L. Balls' xanthogenate method[7] is seen to consist almost entirely of well-matured fibres, whereas the "fly," which constitutes a large proportion of cotton waste, consists mostly of immature fibres, and the waste also contains much fibre damaged by the attack of bacteria or chemicals.

American nitrocellulose powder is made from the short fibre cotton that remains on the seed after the lint has been removed. Except in the case of the high-class cottons, Egyptian and Sea Island, some 10% of "fuzz" remains thus on the cotton seed. A further quantity of short fibre can be removed by suitable mechanical appliances and this is known as "linters," but there is still some more fuzz adhering to the hull, from which it can only be removed after decortication.[8] In order to free the hull fibre from particles of husk it is necessary to subject it to a very drastic treatment with caustic soda under a pressure of 100–110 lb. per sq. in., and then with bleaching powder. Husk residues can also be removed by a process of fermentation, but this must have an even worse effect on the cellulose. Both linters and hull fibre, but especially the latter, are also liable to be injured by exposure to the weather before

[6] *Times*, Sept. 12, 1919.

[7] *Proc. Roy. Soc.*, 1919, **B 90**, 542; *Ann. Repts.*, 1919, 114.

[8] E. de Segundo, *J. Roy. Soc. Arts*, 1919, 67, 184; *J.*, 1918, 118T; 1919, 185A. J. Wallace, *Paper*, 1919, 34; *J.*, 1919, 569A. E. C. Worden, "Technology of Cellulose Esters," 1921, Vol. I., 579. O. Kress and S. D. Wells, *Pulp and Paper Mag.*, 1919, 697, 726; *J.*, 1919, 858A.

they are removed from the seed, so that the materials cannot be considered as really suitable for making stable explosives, unless precautions be taken to prevent such deterioration.

In Germany and Austria the supply of cotton waste and linters began to fail early in the war in consequence of the blockade. First they fell back on cotton and linen rags and when the supply of these also became inadequate they adopted the use of wood cellulose, preliminary experiments on which had been done before the war.[9] Thin tissue paper manufactured by the Ritter-Kellner modification of the sulphite process is the most suitable. It is used in the form of flakes 5–10 cm. across and of such a thickness that a square metre would weigh 18–22 g.[10]

Nitration.

In England Thomson's displacement process is generally used, and it has also been adopted in France to a considerable extent, but in America a different method has been worked out by Du Ponts and a plant on this system was erected at Irvine in Scotland for the manufacture of the nitrocotton for the nitrocellulose powder. It was also used in Germany. The process is a development of the Ardeer direct dipping method but it has been possible to dispense with much of the hand labour by the adoption of short-fibre cotton, such as linters and hull fibre. The plant is erected in a building of 4 floors,[11] the top one being occupied by the motors, the one below by the nitrating tanks or dippers and measuring vessels for the acid, the ground floor by the centrifugals, and the basement by the drowning tanks. A unit consists of one measuring tank, four dippers, one centrifugal, and one drowning tank, and a standard nitrating house contains nine of these units. The dipper is a cylindrical steel vessel about 30 in. in diameter and 48 in. deep with a conical bottom, fitted with a cover, a double mechanical stirrer, and a wooden fume shaft. The charge consists of 30 lb. of cotton and 1500 lb. of mixed acid, which are fed in simultaneously, the operation occupying 2 minutes. For soluble cotton the time of nitration is about 20 minutes and the stirrer is kept going the whole time. The charge is run through a 6-in. pipe into the centrifugal below, which is rotated slowly until the whole has been received, when the speed is increased to 1150 r.p.m. and kept at that for about 5 minutes. The contents are then discharged by means of forks through the bottom into the drowning tank, whence the nitrocellulose is carried by the water to the pump-house from which it is pumped to the boiling house.

[9] See *Ann. Repts.*, 1919, 538, 559; 1920, 538.

[10] For a specification of the material and other information see R. Schwarz, *Oesterr. Chem. Zeit.*, 1919, 50; *J.*, 1919, 662A.

[11] Worden, "Technology of Cellulose Esters," 1921, Vol. I., 1994–2001.

Stabilisation.

The principal object of boiling both the cellulose and the nitrocellulose is to decompose and remove unstable products. The stabilisation is also assisted by reducing the product to a pulp in a beater. A type of beater much used in America is the Miller duplex beating engine, which has two bed plates fitted with stationary knives, one below and the other above the rotating knife roll.[12] Worden states that the addition of a minute amount of a nitrocellulose solvent, such as 0·1% of acetone, to the water in the beater decreases materially the time of beating. The Jordan engine is also used to reduce still further the state of division of the pulp, and then it is sometimes forced through a screen and the particles that are retained are returned to the beater. If the pulping be excessive, however, it increases the solubility in ether-alcohol.

Drying.

When the nitrocellulose is to be gelatinised by means of ether-alcohol the use of stoves for drying may be avoided by displacing the water with alcohol, and this method was used at Pembrey as also at numerous Continental and American factories, but at Gretna it was dried in Quinan stoves. A drying house on this principle contains a number of bays separated from each other by walls. In each is a shallow tinned iron pan in which a perforated diaphragm is supported on felt strips. On this is placed a piece of fabric on which about 33 lb. of wet nitrocotton is spread evenly and then a silk screen supported on a wooden frame is placed over it. Hot air at a temperature of about 65° C. is blown through for 48 min., then cold air for 9 min., and the dry product is ready to be unloaded. The entire operation takes an hour and the operatives pass up and down the building unloading and reloading each pan in turn. The floor is kept wet. The consumption of steam at about 100 lb. per sq. in. in the heaters was 2·433 lb. per lb. of dry nitrocotton produced, or, as the wet material contained about 32% of moisture, 5·6 lb. per lb. of water evaporated.[13]

Viscosity.

A considerable amount of work has been done on the viscosity of the colloidal sols of cotton and nitrocotton, especially in England. It has long been recognised how important this property of viscosity is in most of the industries in which cellulose or a derivative of it is used in conjunction with a solvent, but progress has been impeded by the difficulty in obtaining concordant results with cotton dissolved in cuprammonium solution or other solvent, and the

[12] *See* E. C. Worden, *op. cit.*, pp. 2086–2090.
[13] "H.M. Factory, Gretna, Description of Plant and Processes," p. 138.

consequent doubt as to whether the figures obtained really represented the nature of the colloid under examination. Preliminary experiments had been made in England as in other countries before the war, but these had not led to any very definite conclusions. During the war difficulties in obtaining uniform results in the manufacture of cordite R.D.B. and the need for economy in the use of solvents led to fresh investigations by a considerable staff of chemists in the Research Department, Woolwich Arsenal, and the Department of Explosives Supply of the Ministry of Munitions, and determinations of viscosities became part of the routine in the mills where the cotton was prepared. Many of the results of these researches have now been published. W. H. Gibson and L. M. Jacobs describe the falling sphere viscosimeter that is used,[14] and for the examination of solutions of nitrocotton, and Gibson gives the dimensions of the narrower tube that is employed for the deeply coloured solutions of cotton in cuprammonium.[15] In this they arrived at a different conclusion to E. F. Higgins and E. C. Pitman in America, who preferred the Stormer rotating disc viscosimeter on the ground that it is available over a greater range of viscosities.[16] L. Spencer and R. McCall give the special precautions that are recommended to ensure concordant results, but do not describe the latest method for the preparation of the solution. The liquid must contain definite proportions of copper and ammonia and the solution of the cotton must be protected from light and air, both of which rapidly reduce the viscosity.

The results obtained by the application of these methods are discussed at some length by R. A. Punter,[17] but they might with advantage have been expressed more clearly. A fairly close relationship was traced between the viscosities of the solutions of the cotton and of the nitrocotton. Both are affected greatly by the boiling processes. To obtain cotton which gives a uniformly low viscosity it is necessary to subject it to a drastic treatment with caustic soda in the kier under high pressure. The initial proportion of caustic soda to water should not be less than 3%, the pressure should be at least 40 lb. per sq. in. and preferably 70 or 80, the time of treatment at least 10 hours. Cotton that had been kiered at 40 lb. pressure was found on nitration to give less unnitrated fibre than that which had been treated at lower pressures. The omission of the bleaching and souring processes makes no difference to the viscosity. In the case of linters as used for the manufacture of nitrocellulose powder by Du Pont's method, it was found advis-

[14] *Chem. Soc. Trans.*, 1920, **117**, 473; *J.*, 1920, 558A; *Ann. Repts.*, 1920, 539.

[15] *Ibid.*, 479.

[16] *J. Ind. Eng. Chem.*, 1920, **12**, 587; *J.*, 1920, 541A.

[17] *J.*, 1920, 333T.

able to have the pressure in the kiers at least 70 lb. per sq. in., probably because this material contains a larger proportion of cutocellulose which is only attacked slowly by the caustic alkali. Nitrated cotton which has not been boiled gives solutions of very high viscosity, but this falls during the boiling at first rapidly and then more slowly.

A study of the viscosities of solutions of nitrocellulose in ether-alcohol has been published by W. H. Gibson and R. McCall.[18]

These researches were rediscussed by Sir R. Robertson in a paper read before a joint meeting on colloids held by the Faraday Society and the Physical Society on October 25, 1920,[19] and also by F. Sproxton, who ascribes the lower viscosities of solutions containing a small proportion of water to the affinity of the hydroxyl groups of the cellulose molecule for water. They have also a considerable affinity for alcohols and especially for ketones. Sproxton deals with the question more from the point of view of the manufacture of celluloid. G. Barr and L. L. Bircumshaw gave the results of viscosity measurements on solutions of cellulose acetate. In these also the addition of water to solutions in acetone causes the viscosity to fall to a well-defined minimum at about 6·5% water, and further additions cause it to rise again. The admixture of alcohol to the acetone also causes the viscosity to fall but not to rise again. Benzene, on the other hand, causes a steady rise of the viscosity.

W. K. Tucker deals with the question of the viscosity of nitrocellulose solutions from the point of view of the manufacture of artificial leather in the United States.[20] He also uses a falling sphere viscometer but with a steel ball, $\frac{5}{8}$ in. in diameter. The time of fall of 10 in. in the solutions used varies from 5 to 60 seconds. He states that the solvents used are either acetone oil or ethyl acetate, which however, are mixed with a considerable proportion of a non-solvent such as benzene or benzine, which increases the viscosity. Formerly it was considered necessary to have present a proportion of a high-boiling solvent, such as amyl acetate or ethyl propionate, but most manufacturers now do without this, and some state that such a solvent tends to make pinholes in the finished product. High-boiling solvents give more viscous solutions than ethyl acetate. The presence of alcohol in these solutions tends to reduce the viscosity.

Propellants.

An account of the development of German smokeless powders during the war has been given by O. Poppenberg.[21] Even before

[18] *J.*, 1920, 172T.

[19] *See J.*, 1920, 376R. The papers have since been published in the form of a Report by the Dept. of Scientific and Industrial Research.

[20] *J. Ind. Eng. Chem.*, 1921, **13**, 623; *J.*, 1921, 654A.

[21] Schwarte's "Die Technik im Weltkriege," 1920.

the war the Germans used for military and naval purposes powders varying greatly both in composition and form. Whereas we employed cordite for every variety of firearm and pressed it all through dies into cord or tube form, and the French used a nitrocellulose powder, poudre B, in strip form, and the Americans another sort of nitrocellulose made into perforated cylinders, the Germans had both nitroglycerin and nitrocellulose powders made into flakes, rings, cubes, tubes, and stars.

For making nitroglycerin powders a variety of nitrocellulose was preferably used that gave on gelatinisation with nitroglycerin a gel of comparatively low viscosity, the so-called "PE-Wolle" nitrated at a high temperature. Before the war these were gelatinised with 20% of acetone obtained as a by-product of the wood distillation industry. As this source of supply did not suffice, ethyl acetate was largely used during the war, but this also required acetic acid for its manufacture. Increased supplies of both these solvents were obtained from the oxidation of acetylene according to the patents of the Hoechst, Griesheim, and Alexander Wacker companies.

Much of the powder in flake form was, however, made without the use of volatile solvents by incorporating the nitrocellulose and nitroglycerin together in the presence of water between hot rolls.

In consequence of the great scarcity of fats during the war every effort was made to substitute other materials for nitroglycerin. Before the war a process had already been worked out by the Köln-Rottweil powder works for the use of trinitrotoluene. In order to obtain the same ballistics they employed a nitrocellulose of somewhat higher nitration than is generally used in Germany for nitroglycerin powders. They gelatinised the powder beneath heated rolls under high pressure and also shaped it at high temperature and pressure. In this way either part or the whole of the nitroglycerin was replaced, but the processes were not free from danger and there were numerous accidents.

Attempts were also made to substitute dinitroglycol for nitroglycerin. The starting point for this synthesis was alcohol, which was first converted by means of chlorine and hydrochloric acid into dichloroethylene; this was then saponified to glycol, which could be nitrated in the same way as glycerin. But great difficulties and delays were experienced in starting this manufacture, and when it was finally got going it was found that dinitroglycol was not really suitable for powder manufacture on account of its volatility, which caused it to have a bad physiological effect on the workers. It was, however, used to a considerable extent for the manufacture of explosives for mining purposes. Eventually the supply of glycerin was increased largely by the fermentation of

sugar, the process being developed by the Protol Company from the discoveries of Connstein.[22]

The tubular powders for the larger guns generally contained mineral jelly, and powders of this type and also in flake form frequently had additions of urea derivatives such as Centralite or Akardite as stabilisers and additional gelatinisers. Sometimes these were used merely to treat the surface and so influence the initial rate of burning.

The nitrocellulose powders sometimes contained these same urea derivatives and sometimes diphenylamine. For rifle powder the surface of the grains was treated with camphor. When the supply of this material from Japan was cut off synthetic camphor made from turpentine was used, but turpentine also became scarce towards the end of the war and Centralite was used instead. Some samples of powder for 15-cm. guns used in the land service contained nitrotoluenes, probably added for the same purpose.

The nitrocellulose powders were gelatinised with ether-alcohol obtained by the fermentation of potatoes, and as all foodstuffs were scarce it was necessary to exercise great economy and to recover as much as possible, not only from the drying stoves, but also by drawing away the air from the neighbourhood of the presses and absorbing the alcohol and ether in sulphuric acid towers and finally with charcoal. It was thus possible to cut down the consumption of alcohol from 168 to 135 kg. per 100 kg. of powder.

Nitrocellulose powders were always used for small arms and field guns, the nitrocellulose being often a blend of 3 parts of high-nitrated cellulose almost insoluble in ether-alcohol and 1 part of low-nitrated soluble nitrocellulose. For naval guns nitroglycerin powder in tube form was used, but when the same guns were adapted for use on land a nitrocellulose powder in tube form was sometimes substituted. For howitzers nitroglycerin powders of the ballistite type in flake form were employed, and it was principally in these powders that liquid trinitrotoluene was substituted for part of the nitroglycerin. In this respect their practice differed fundamentally from ours, as we often used nitrocellulose powders of the American type for our howitzers.

Ammonpulver.

The Germans also used a propellant made by incorporating 85% of ammonium nitrate with 15% of charcoal and compressing it into large pellets having a density of about 1·4. This was practically the same as a powder that was used by the Austrians from 1890 to 1896 for guns of various calibres, but was given up again by them in favour of ballistite.[23]

[22] See *Ann. Repts.*, 1919, 296, 442; 1920, 427, 537.

[23] *See* J. Mayr, *Z. ges. Schiess- u. Sprengstoffw.*, 1907, 401; P. Rusch, *Mitt. Seewesen*, Jan., 1909; *ibid.*, 1909, 73; also *Ann. Repts.*, 1920, 557.

The most serious objection to it seems to have been that on storage the pellets were liable to undergo changes which caused their partial disintegration and the consequent generation of high pressures in the gun, and if left in a hot gun similar changes took place, especially if the ammonpulver were damp. These changes were due to the changes in the crystalline form of ammonium nitrate, especially the one at 32° C. The Germans overcame this fault to a considerable extent by using composite charges only a third or a half of which was ammonpulver, the remainder being ordinary smokeless powder. The powder was kept dry either by placing it in a metal cartridge case closed with a cork or a bung of compressed peat in the case of fixed ammunition, or by enclosing it in a box made of nitroglycerin powder.

Early in the war the ammonpulver was made by the ordinary black powder process: incorporation under edge runners, pressing, breaking down, and pressing again. Later the incorporation was carried out by mixing with water, which was then evaporated off on a heated rotating drum, but it was still necessary to press twice. But finally a method was worked out by the Krause-A.-G. of Munich whereby one of the pressings was avoided. The finely-divided charcoal was suspended in a solution of ammonium nitrate which was reduced to a mist by means of a centrifugal disc, and the droplets were made to fall down a tower where they met an ascending stream of hot air. The granules were removed continuously from the base of the tower and were pressed automatically into hollow cylinders.

The principal motive for the adoption of this powder was to save the large amount of alcohol that is required for the manufacture of nitrocellulose powder, but it also possesses virtues of its own: in consequence of its low temperature of explosion it erodes the guns very little, and for the same reason it gives little or no muzzle flame.[24]

American Powders.

An account of the development of the smokeless powders for the United States Army and Navy is given by E. C. Worden.[25] He states that a process has recently been invented for drying the multi-tubular nitrocellulose powder whereby the time required has been reduced from several weeks to one or two days, but the nature of the method has not been made public. The full discussion of explosives containing cellulose nitrates will, however, form the subject matter of Vol. VII. of this monumental work, and Vol. IX., now in the press, is to be a bibliography of explosives.

24 O. Poppenberg, "Die Technik im Weltkriege," 1920, 104.

25 "Technology of Cellulose Esters," Vol. I., pp. 2928-2942.